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A Study of the Volatility of the Metal Chelates of Dipivaloylmethane and Related Dicarbonyl Compounds.

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A STUDY OF THE VOLATILITY OF THE METAL CHELATES OF DIPIVALOYLMETHANE AND RELATED DICARBONYL COMPOUNDS

A Dissertation

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To Saint Frances Xavier Cabrini

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ABSTRACT

The purpose of this study was to evaluate the volatility of a representative number of metal chelates of dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione) and to determine their separability by fractional sublimation. The volatilities of typical metal chelates of this ligand were compared with those of the corresponding metal chelates of other β-dicarbonyl ligands. The study included the preparation of the metal chelates of these ligands and their characterization by physical methods.

The volatility and separability of the metal chelates were studied at low pressure using a Berg fractional sublimator that provided a condensation temperature gradient which was the selective factor in the separations.

A modified version of the Berg sublimator was prepared and a preliminary evaluation was done on its potential as a tool for separating volatile mixtures of the chelate.

The quantitative evaluation of the sublimation separability of metal chelate mixtures was done by comparing the various individual condensation temperature zones of pure chelates produced during sublimation and by subliming synthetic mixtures of the chelates and determining the extent of overlap of condensation temperature zones. Selected mixtures were evaluated by visible absorption spectrophotometry.

The following metal chelates of dipivaloylmethane were studied: Al(III), Ba(II), Be(II), Ca(II), Cd(II), Ce(IV), Co(II), Co(III), Cr(III), Cu(II), Dy(III), Er(III), Fe(III), Gd(III), Hg(II), Ho(III), La(III), Lu(III), Mg(II), Mn(III), Nd(III), Ni(II), Pd(II), Pr(III), Pt(II), Rh(III), Sc(III), Sm(III), Sr(II), Tb(III), Th(IV), Tm(III), Y(III), Yb(III), Zn(II), Zr(IV). The metal chelates of members of group IIA were not volatile except for beryllium and magnesium. Among all the metal chelates studied, the beryllium chelate was the most volatile. The volatilities of the actinide and lanthanide metal chelates were found to be less than those of the other metal chelates. No definite volatility trend was found when comparing the temperature of the sublimation-condensation zone of the metal chelates of dipivaloylmethane and those of the other ligands.

A previously unstudied ligand, malonaldehyde (1,3-propanedial) was prepared, its metal chelates were characterized, and their volatilities were compared to those of the other ligands studied. Unfortunately, the metal chelates of malonaldehyde proved to be difficult to isolate due to the reactive and unstable nature of the ligand. A significant observation made in this study was that the palladium chelate of this ligand decomposed partially under low temperature and pressure sublimation to give a smooth palladium mirror.

A simple system was prepared for the gas phase oxidation of 1,3-propanediol to malonaldehyde. The system provided a method of exposing the alcohol vapors to a reactant or catalyst in a horizontal metal chamber. Studies indicated that dehydration and fragmentation

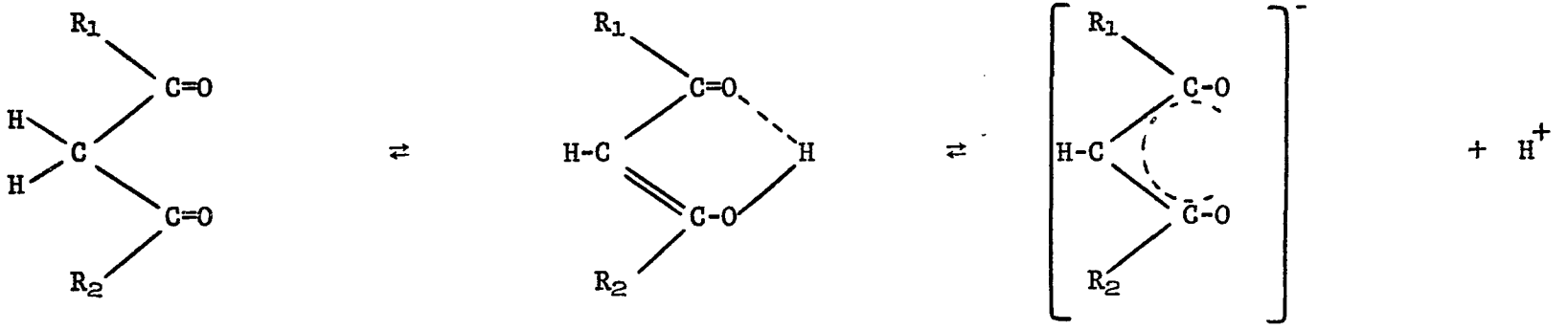
were taking place along with oxidation. The reaction mixtures were characterized by gas chromatography and ultraviolet absorption spectrophotometry.

INTRODUCTION

The study of β-dicarbonyl type compounds is a fruitful area of research because these chemical species have proven their versatility and usefulness in the separation and identification of metal ions (1-4). In the field of organic chemistry these compounds have been useful as intermediates for organic synthesis (5-7) and as NMR shift reagents (8-12).

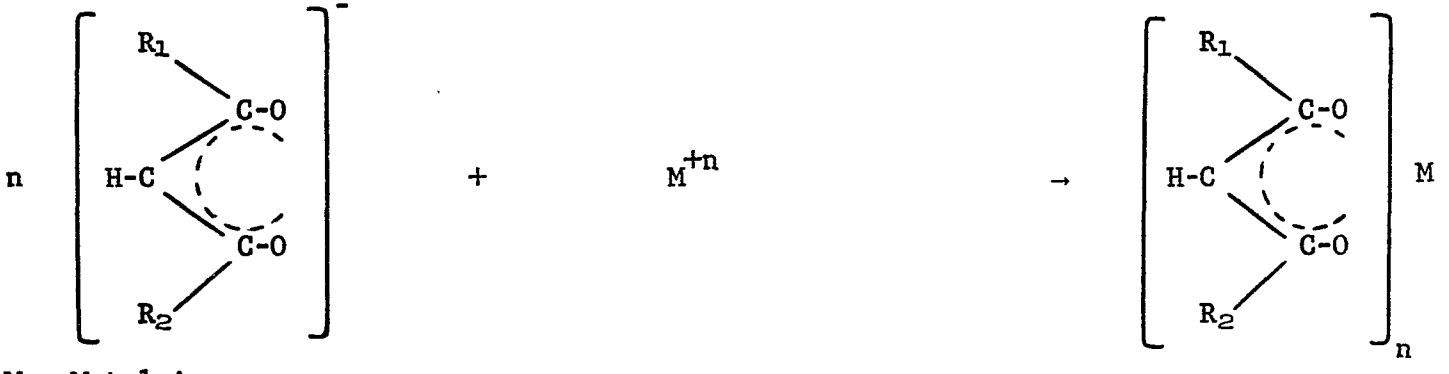
The studied β-dicarbonyls exist as tautomers in a keto-enol equilibrium which is illustrated in Figure 1. Chelation with metal ions takes place in the enol form as illustrated in Figure 1. The structural formula, trivial name and systematic name of each of the ligands mentioned in this study are given in Table I along with the symbol chosen to represent that ligand throughout this work.

The research group under the direction of Dr. E. W. Berg has studied for many years the preparation, uses and volatility of β-diketone ligands and their metal chelates. Truemper (13) determined the vapor pressure-temperature curves and sublimation temperatures of a series of β-diketone metal chelates and suggested the possibility of separating these compounds by gas-liquid chromatography and by sublimation. Dowling (14) studied the volatility of some cobalt (III) and iron (II) β-diketone chelates. Berg and Hartlage (15) designed a metal fractional sublimator which will be referred to throughout this work as the Berg sublimator. This sublimator used a continuous temperature gradient as the selective factor in the separation of the



Keto form Enol form Dissociated form

R_1,R_2: Any alkyl, aryl, heterocyclyl group or hydrogen.



M: Metal ion

n: Number of moles of ligand and oxidation number of the metal

FIGURE 1. β-Dicarbonyls and Their Metal Chelates

TABLE I

β-Dicarbonyl Compounds Used in This Study

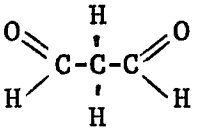
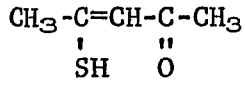
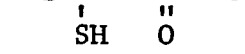
Trivial Name and Structural Formula	Systematic Name	Adopted Symbol
Malonaldehyde or malondialdehyde 	1,3-Propanedial	MDA
Acetylacetone $CH_3-C(=O)-CH_2-C(=O)-CH_3$	2,4-Pentanedione	AA
Dipivaloylmethane $t\text{-}C_4H_9-C(=O)-CH_2-C(=O)-C_4H_9\text{-}t$	2,2,6,6-Tetramethyl-3,5-heptanedione	DPM
Trifluoroacetylacetone $CF_3-C(=O)-CH_2-C(=O)-CH_3$	1,1,1-Trifluoro-2,4-pentanedione	TFAA
Hexafluoroacetylacetone $CF_3-C(=O)-CH_2-C(=O)-CH_3$	1,1,1,5,5,5-Hexafluoro-2,4-pentanedione	HFAA
Benzoyltrifluoroacetone $C_6H_5-C(=O)-CH_2-C(=O)-CF_3$	1-Phenyl-4,4,4-trifluoro-1,3-butanedione	BTFA
Thenoyltrifluoroacetone $C_4H_3S-C(=O)-CH_2-C(=O)-CF_3$	1,1,1-Trifluoro-4-(2-thenyl)-2,4-butanedione	TTFA

TABLE I (cont'd)

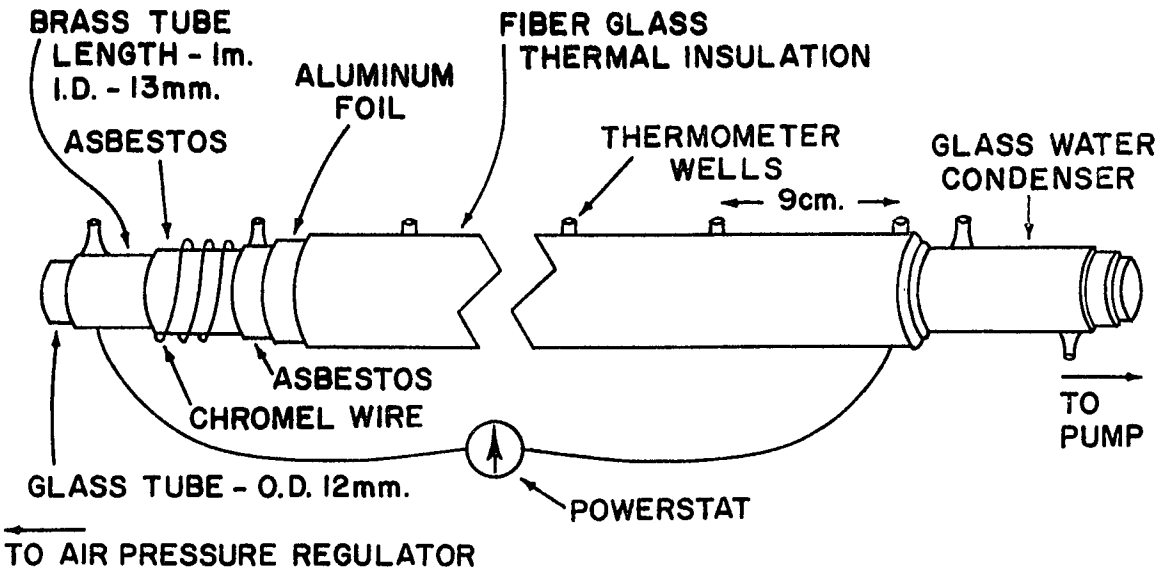
Trivial Name and Structural Formula	Systematic Name	Adopted Symbol
Thioacetylacetone 	4-Mercaptopent-3-en-2-one	SAA
Thiothenoyltrifluoroacetone 	1,1,1-Trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-4-one	STTFA
Thiohexafluoroacetylacetone 	1,1,1,5,5,5-Hexafluoro-4-mercaptopent-3-en-2-one	SHFAA

volatile metal chelates. Hartlage (16) did an extensive survey of the volatility and separability of β-diketone metal chelates by fractional sublimation. He proved quantitatively that data on the individual sublimation-condensation temperature zone could be used to predict the separation of mixtures by this method. Chiang (17) extended this survey to include the β-diketone metal chelates of Group IIIB elements. Reed (18) studied the preparation of thio-β-diketones and methylene alkylated β-diketones as well as the volatility and separability of selected metal chelates.

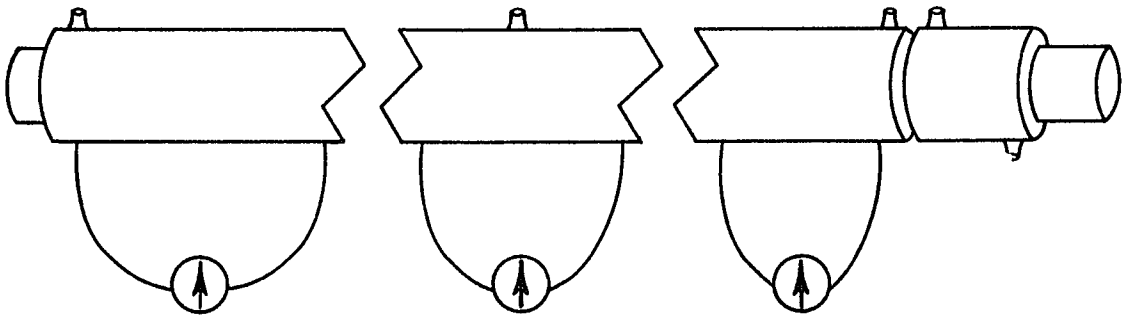
The present study was undertaken to extend our knowledge of β-dicarbonyl compounds and their metal chelates. First it was decided to determine the volatility and separability of the metal chelates by fractional sublimation. During this investigation a modified version of the Berg sublimator was assembled and evaluated in terms of its ability to separate chelate mixtures. The sublimators are shown in Figure 2.

This investigation concentrated on the study of dipivaloylmethane because of the importance of this ligand, and its analogs, to analytical chemistry. Previous studies (4,13,16,17) proved that some of the metal chelates of this ligand are volatile and can be used to separate metals which had proven difficult to separate by conventional methods. The metal chelates of this ligand are the ones which currently are used as NMR shift reagents (12,19-23).

To find an economical way to prepare dipivaloylmethane it was decided to attempt its preparation from malonaldehyde via a Grignard



BERG FRACTIONAL SUBLIMATOR[a]



LARGE FRACTIONAL SUBLIMATOR[a] - 2m.

[a] NOT TO SCALE

FIGURE 2. FRACTIONAL SUBLIMATORS

type synthesis (24). The synthesis involved as its first step the oxidation of 1,3-propanediol in the vapor phase. Catalytic oxidation of volatile alcohols has been studied extensively since the early part of this century when Sabatier (25) prepared aldehydes from primary alcohols. Many industrial and laboratory systems have been designed to accomplish these reactions (5,6,26,27) but they used expensive or complicated equipment and chemicals. The oxidation system proposed in this dissertation involves inexpensive equipment and chemicals.

The new oxidation system produced malonaldehyde in a complex mixture which made the proposed synthesis impractical. At this point the investigation was directed to the study of malonaldehyde as a ligand.

Malonaldehyde is a compound of special interest to food chemists and biochemists (28-32) because its presence can be related to the oxidation of polyunsaturated fatty acids. Recently Pryor (33) mentioned the role of malonaldehyde as an indicator for the peroxidation of lipids in tissue. This compound was first recognized by Claisen (34) who prepared it in aqueous solution by the hydrolysis of β-ethoxyacrolein. Later Hüttel (35) isolated the pure compound from its sodium enolate. He described the white solid as being volatile, hygroscopic and very reactive. This compound is currently produced by the hydrolysis of its bis-(diacetal)s (36-38). Malonaldehyde produced by this method often gives complex mixtures (36,39).

Metal chelates of malonaldehyde have been used as models for the LCAO-MO calculations (40) of the enol form of acetylacetone and

its metal complexes but the chromium (III) chelate has been the only (41) member of this family which has been isolated and reported. Kwon (32) postulated the presence of the iron (III) chelate of malonaldehyde but reported he could not isolate the compound.

The last phase of this work involved the study of the metal chelates of malonaldehyde.

EXPERIMENTAL DATA AND RESULTS

I. Source of Chemicals

Acetylacetone: This commercial reagent was supplied by Matheson, Coleman and Bell and was purified by distillation.

Copper Turnings: These reagent grade turnings were supplied by J. T. Baker Chemical Company and used without further purification.

Copper (II) Oxide Wire: This commercial reagent was supplied by J. T. Baker Chemical Company and used without further purification.

Sodium N,N-Diethyldithiocarbamate Trihydrate: This reagent grade chemical was supplied by Eastman Organic Chemicals and used without further purification.

Dipivaloylmethane: This reagent grade chemical was supplied by Peninsular Chemical Research, Inc. and used without further purification.

Platinum Metals Salts: These reagent grade chemicals were supplied by A. D. Mackay, Inc. and used without further purification.

1,1,3,3-Tetramethoxypropane: This chemical, 99+% pure, was supplied by Aldrich and was distilled twice at reduced pressure before it was used.

Water: All water used in this study was first distilled and then deionized.

Other Chemicals Used: All other chemicals came from normal suppliers and were of Analytical Reagent Grade.

II. Apparatus and Measurements

Carbon and Hydrogen Analysis: These analyses were performed at Coates Laboratories, Baton Rouge, Louisiana by Mr. R. L. Seab.

Melting Point Measurements: The melting point values were observed using a capillary tube in a Mel-Temp melting point apparatus.

Gas Chromatography: The qualitative gas chromatographic data were obtained in a Beckman GC-5 instrument, equipped with the flame detector and a Teflon coated, 10' x 1/8" aluminum column packed with Carbowax 20M; and in a Glowal 320 instrument, equipped with a flame detector and a 6' x 1/8" glass column packed with 15% SE 30 on Chromosorb W, mesh 60/80. The quantitative data were obtained in an Aerograph 90 instrument equipped with a thermal conductivity detector and a 10' x 1/8" aluminum column with Carbowax 20M.

Infrared Spectroscopy: The infrared spectra were obtained on a Perkin-Elmer Infracord spectrometer. All samples were powdered and suspended in potassium bromide pellets.

Nuclear Magnetic Resonance Spectroscopy: The NMR spectra were run on a Varian A-60A spectrometer. The samples were run as saturated solutions in carbon tetrachloride at ambient temperature of the probe, unless otherwise specified.

Visible and Ultraviolet Absorption Spectroscopy: The visible and ultraviolet data were obtained in a Beckman DB spectrophotometer equipped with a Sargent model SRL recorder.

Fractional Sublimators: The fractional sublimators used were designed by the author and built in the machine shop of the Coates Laboratory at Louisiana State University.

Metal Oxidation Chamber: The metal chamber was designed by the author and built in the machine shop of St. Bernard College, Cullman, Alabama.

III. Preparation and Characterization of β-Dicarbonyl Metal Chelates

Preparative procedures for a number of β-diketone chelates have been reported in the literature (4,15,42-48). In this dissertation, only the procedures not reported earlier have been described.

The metal chelates prepared were characterized by melting point, carbon and hydrogen analysis, infrared and NMR spectroscopy.

1. Acetylacetonates

Bis-(acetylacetonato)palladium (II). This chelate was prepared by the method suggested by Hartlage (16) and was purified by sublimation. The elongated yellow crystals sublimed with partial decomposition at 190°C.

Analysis: Calculated for $PdC_{10}H_{14}O_4$; C, 39.43%; H, 4.62%. Found: C, 39.47%, H, 4.94%.

Tris-(acetylacetonato)chromium (III). This chelate was prepared by the method suggested by Hartlage (16) and was purified by sublimation. The purple, plate-like crystals melted at 215-217°C. This was in agreement with the value reported by Hartlage which was 215-218°C. The infrared spectrum of this compound was identical to that of the compound prepared by Hartlage.

2. Dipivaloylmethanates.

The various dipivaloylmethanates prepared in this study are listed in Table II along with some of their physical properties and an indication of the method employed for their preparation. Many of these chelates were prepared by common methods (16,42) used in the preparation of other β-diketone chelates. These methods referred to in Table II are described briefly below.

Method A (16): A 15% dipivaloylmethane-ethanol solution was added while stirring to an aqueous solution of the metal salt which had been buffered with an excess of potassium acetate. The chelate was recovered by filtration and purified by sublimation,

Method B (42): Pure dipivaloylmethane was added to a 50% ethanol-water solution of the metal salt, then concentrated aqueous ammonia was added while stirring until the chelate precipitated. The chelate was recovered by filtration and purified by recrystallization from aqueous ethanol.

TABLE II

GENERAL DATA ON THE METAL CHELATES OF DIPIVALOYLMETHANE[1]

Compound	Crystals	Method of Preparation	m.p. [lit. (42)] °C	Formula	Analysis Calculated C%	Calculated H%	Found C%	Found H%
$Al(DPM)_3$	white needles	A	265-266[264-265]	$AlC_{33}H_{57}O_6$	68.72	9.96	68.29	9.95
$Ba(DPM)_2$	white needles	B	171-172[171]	$BaC_{22}H_{38}O_4$	52.44	7.60	----[c]	----[c]
$Be(DPM)_2$	white needles	B	95-97[93-97]	$BeC_{22}H_{38}O_4$	70.36	10.20	70.20	10.28
$Cd(DPM)_2$	white needles	C	228[a]	$CdC_{22}H_{38}O_4$	55.17	8.00	54.97	8.05
$Cr(DPM)_3$	purple	D	228-229[229]	$CrC_{33}H_{57}O_6$	65.86	9.77	65.56	9.67
$Co(DPM)_2$	purple	B	142-143[143]	$CoC_{22}H_{38}O_4$	62.10	9.00	60.14	9.14
$Co(DPM)_3$	dark green	A	244-245[245]	$CoC_{33}H_{57}O_6$	65.11	9.45	65.17	9.63
$Cu(DPM)_2$	deep blue	A	198-199[198]	$CuC_{22}H_{38}O_4$	61.44	8.91	61.00	8.81
$Fe(DPM)_3$	red needles	A	164-165[163]	$FeC_{33}H_{57}O_6$	65.44	9.48	64.67	9.46
$Mg(DPM)_2$	white needles	B	94-95[94]	$MgC_{22}H_{38}O_4$	67.60	9.80	----[c]	----[c]
$Mn(DPM)_3$	black	C	164-165[165]	$MnC_{33}H_{57}O_6$	65.54	9.50	65.32	9.56

Compound	Crystals	Method of Preparation	m.p. [lit. (42)] °C	Formula	Analysis Calculated C	H	Found C	H
$Ni(DPM)_2$	pink needles	B	223-225[225]	$NiC_{22}H_{38}O_4$	61.84	8.96	60.99	9.17
$Hg(DPM)_2$	white needles	A	190-192[192]	$Hg_2C_{22}H_{38}O_4$	34.39	5.01	34.04	4.97
$Pd(DPM)_2$	yellow	C	228[b]	$PdC_{22}H_{38}O_4$	55.86	8.10	55.77	8.19
$Pt(DPM)_2$	yellow	C	230[b]	$PtC_{22}H_{38}O_4$	47.05	6.54	46.98	6.81
$Rh(DPM)_3$	orange yellow	C	185	$RhC_{33}H_{57}O_6$	61.19	8.79	64.10	9.50
$Sr(DPM)_2$	white needles	B	199-201[200]	$SrC_{22}H_{38}O_4$	58.18	8.43	-----	----
$Zn(DPM)_2$	white needles	B	143-144[144]	$ZnC_{22}H_{38}O_4$	60.89	8.82	60.90	8.82
$Zr(DPM)_4$	yellow orange	A	330-332	$ZrC_{44}H_{76}O_8$	64.09	9.31	63.85	9.34

[a] Decomposes

[b] Sublimes with partial decomposition

[c] Erratic values.

Method C - A 10% aqueous solution of potassium hydrogen carbonate was added to a 5% aqueous solution of the metal salt until the solution reached a pH just below that required for the precipitation of the hydroxide. This solution was then treated with a slight excess of a 15% dipivaloylmethane-ethanol solution and stirred for five hours. The chelate was recovered by filtration and purified by sublimation.

Method D (42) - A solution of three grams of chromium (III) chloride hexahydrate, twenty grams of urea and five grams of dipivaloylmethane in a 65% ethanol-water solvent was heated at 90°C for five hours. The solution was cooled to room temperature and 100 ml of water was added. The chelate was recovered by filtration and purified by sublimation.

Other Chelates of Dipivaloylmethane. The other chelates of dipivaloylmethane used in this study were prepared by Chiang (17) and were supplied to the author by Dr. E. W. Berg.

3. Malonaldehydates.

Bis-(malonaldehydato)palladium (II). This chelate was prepared by treating the aqueous solution of malonaldehyde, produced from the acid hydrolysis of tetramethoxypropane, with 5N sodium hydroxide until the solution reached a pH of 5.1. This slightly acidic solution was then added to an ice cooled suspension of palladium (II) chloride in anhydrous ether. The mixture was stirred for two hours and then allowed to stand for 12 hours. The ether was decanted and dried for two hours with anhydrous magnesium sulfate powder. The mixture was

filtered, and the ether filtrate was concentrated in a rotary evaporator at 30°C until the yellow solid started to precipitate. The precipitate was filtered in a nitrogen atmosphere and dried at 40°C in a vacuum desiccator. The fine yellow needles were then purified by sublimation. (The solid turns gray in air and is finally decomposed to a salt-like compound.) The needles decomposed at 107°C. The compound sublimed at 180°C and 0.5 mm Hg with partial decomposition to a palladium mirror. The yield was 41% after extracting the chelate from the aqueous layer with a total of 400 ml of ether.

Analysis: Calculated for $PdC_6H_6O_4$: C, 28.98, H, 2.44. Found: C, 28.35; H, 2.41.

Tris-(malonaldehydato)chromium (III). This compound as well as the analogous palladium compound was prepared according to the procedure described by Collman (41). The yield was 38% by the Collman method and 31% by the previously described palladium method. The product was purified by sublimation and the red needles melted at 182-183°C. This was in agreement with the value reported by Collman which was 182-183°C.

Analysis: Calculated for $CrC_9H_9O_6$: C, 40.76%; H, 3.42%. Found: C, 41.00%; H, 3.72%.

Attempted Chelation of Other Metal Ions with Malonaldehyde. Attempts were made to chelate the following metal ions with malonaldehyde: aluminum (III), cobalt (II), cobalt (III), copper (II), iron (III), manganese (II), manganese (III), platinum (II) and rhodium (III). None of the products could be identified as a true β-dicarbonyl chelate. In

all cases a reaction was evident because the solution either changed color drastically or the metal ion behavior was changed. For example, no precipitation of the rhodium hydroxide occurred when the pH of the rhodium-malonaldehyde solution was raised to 11.2. The infrared spectra obtained from those solid compounds which were recovered from the aqueous solutions indicated the presence of an organometallic compound. However, the spectra were considerably different from those of the palladium and chromium chelates of this ligand. All the infrared spectra showed both a strong O-H absorption band and a perturbed carbonyl band. This seemed to indicate that a salt-like compound or mixture of compounds may have been formed. Efforts to further purify the solids did not succeed. The carbon and hydrogen analysis values reported could not be correlated with those corresponding to the normal chelates, the enolate nor the gem-diol chelate. The NMR spectra of the rhodium compound, in deuterated water, was almost identical to that of the sodium enolate. The aqueous solutions of aluminum (III), copper (II), iron (III) and platinum (II) were extractable with ether. The ether phase was treated by various chromatographic techniques but no solid was recovered. The data from the chromatographic experiments showed that at least two types of components were present, one which could be eluted with benzene or dichloromethane and another that could be eluted with ethanol.

4. Infrared and NMR Data

The infrared and NMR spectra of various β-diketone chelates have been studied and reported in the literature (45-48). The information concerning the spectra of the prepared chelates of dipivaloylmethane

is presented in Table III. The C=O and C=C infrared stretching vibration assignments shown in Tables III, IV and V are based on the infrared study of β-diketone chelates by Nakamoto (45). The absorption bands indicated in the fingerprint region are included because they were used in the characterization of the chelates. The maxima showed great similarities which were independent of the bound metal: Tables IV and V show the absorption band location for the chelates of palladium (II) and chromium (III) bound to different ligands. Table VI shows the NMR chemical shift values for the metal chelates of dipivaloylmethane prepared and Table VII shows values for chelates of palladium (II) with different ligands.

TABLE III

INFRARED DATA FOR THE METAL CHELATES OF DIPIVALOYLMETHANE

Metal Chelate	Frequency Maxima for Selected Absorption Bands,[a] cm^{-1}										
	C=C	C=O	Fingerprint Region								
$Al(DPM)_3$	1600	1570	1245	1230	1175	1155	974	878	798	763	740
$Ba(DPM)_2$	1590	1575	1240	1225	1175	1130	952	868	792	758	735
$Be(DPM)_2$	1550	1515	1250	1230	1170	1160	986	878	817	763	748
$Cd(DPM)_2$	1590	1570	1245	1225	1180	1135	950	870	792	763	739
$Co(DPM)_2$	1555	1520	1240	1225	1177	1149	968	878	786	753	---
$Co(DPM)_3$	1570	1515	1245	1230	1175	1150	969	878	787	754	---
$Cr(DPM)_3$	1595	1560	1248	1230	1177	1148	965	876	793	760	742
$Cu(DPM)_2$	1570	1540	1248	1230	1177	1150	962	878	798	771	745
$Fe(DPM)_3$	1540	1510	1248	1225	1177	1148	962	875	798	762	740
$Mg(DPM)_2$	1549	1525	1248	1225	1180	1135	960	871	796	763	742
$Mn(DPM)_3$	1570	1525	1240	1220	1175	1135	959	872	793	760	739
$Hg(DPM)_2$	1598	1680	1300	1220	1198	1080 1060	985	884	788	753	686
$Ni(DPM)_2$	1575	1560	1245	1222	1180	1140	957	870	792	763	743
$Pd(DPM)_2$	1540	1540	1245	1225	1180	1140	960	877	794	763	---
$Pt(DPM)_2$	1545	1545	1248	1230	1180	1145	963	879	796	763	---
$Rh(DPM)_3$	1545	1545	1245	1225	1180	1142	958	878	789	757	---
$Sr(DPM)_2$	1590	1560	1249	1225	1185	1138	960	871	795	763	738
$Zn(DPM)_2$	1550	1550	1248	1222	1180	1140	952	875	800	763	744
$Zr(DPM)_4$	1575	1540	1240	1230	1178	1150	970	874	794	762	739

[a] Accuracy of values. 650-1000 ($\pm$ 5 cm^{-1}) and 1000-1700 ($\pm$ 10 cm^{-1}).

TABLE IV

INFRARED DATA FOR REPRESENTATIVE PALLADIUM (II)-β-DICARBONYL CHELATES

Metal Chelates	Frequency Maxima for Selected Absorption Bands[a] cm^{-1}			
	C=C	C=O	M-O and Ring Deformation	M-O
$Pd(MDA)_2$	1590	1590	635	457
$Pd(AA)_2$	1570	1547	697	464
$Pd(DPM)_2$	1540	1540	660	505
$Pd(TFAA)_2$	1610	1597	613	448
$Pd(TTFA)_2$	1576	1543	617	470
$Pd(BTFA)_2$	1600	1577	615	470
$Pd(SAA)_2$[b]	1580	1560	---	505
$Pd(SHFAA)_2$[b]	1545	1521	---	400
$Pd(STTFA)_2$[b]	1540	1517	---	---

[a] Accuracy of values $\pm$ 5 cm^{-1}

[b] Data from Reed (18).

TABLE V

INFRARED DATA[a] FOR REPRESENTATIVE CHROMIUM (III)-β-DICARBONYL CHELATES

Metal Chelate	Frequency Maxima for Selected Absorption Bands[b] cm^{-1}			
	C C	C O	M-O and Ring Deformation	M-O
$Cr(MDA)_3$	1600	1600	692	463
$Cr(AA)_3$	1575	1524	677	459
$Cr(DPM)_3$	1580	1555	648	510

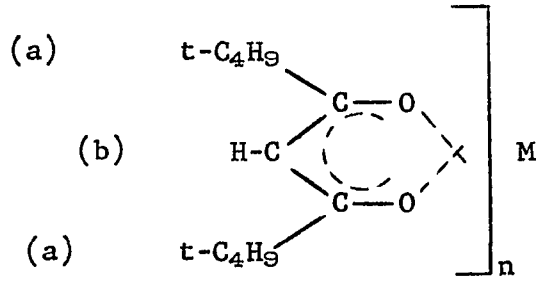
[a]Spectra run in a Beckman IR-10

[b]Accuracy of values $\pm$ 5 cm^{-1}

TABLE VI

NMR Data for Representative Metal

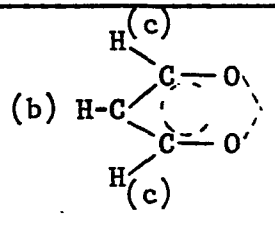
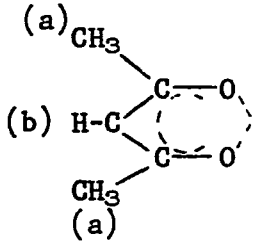
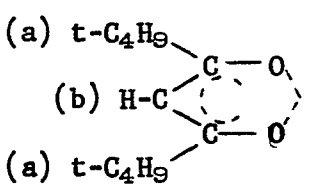
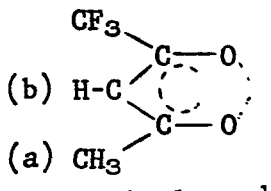
Chelates of Dipivaloylmethane



Metal Chelate	Chemical Shift (δ) ppm (CCl_4)	
	b	a
$Al(DPM)_3$	5.60	1.08
$Ba(DPM)_2$	5.55	1.01
$Be(DPM)_2$	5.80	1.19
$Cd(DPM)_2$	5.72	1.19
$Ca(DPM)_2$	5.60	1.06
$Co(DPM)_2$	5.65	1.10
$Mg(DPM)_2$	5.80	1.19
$Ni(DPM)_2$	5.35	1.17
$Pd(DPM)_2$	5.62	1.15
$Pt(DPM)_2$	5.60	1.14
$Rh(DPM)_3$	5.60	1.13
$Sr(DPM)_2$	5.59	1.05
$Zn(DPM)_2$	5.74	1.21

TABLE VII

NMR DATA FOR REPRESENTATIVE PALLADIUM (II)-β-DICARBONYL CHELATES

Metal Chelate	Chemical Shift (δ) ppm ($CDCl_3$)		
	c	b	a
	7.18 (d)*	5.62 (t)*	
		5.42 (s)*	2.08 (s)*
		5.62 (s)*	1.15 (s)*
		5.90 (s)*	2.25 (s)*

* s = singlet; d = doublet; t = triplet.

IV. Oxidation System for the Conversion of Alcohols to Carbonyl Bearing Compounds

1. Oxidation System and Data

The object of this phase of the investigation was to prepare malonaldehyde in its dicarbonyl form and then react it, in a non-aqueous medium, with tert-butylmagnesium bromide to produce, on hydrolysis, 2,2,6,6-tetramethyl-3,5-heptanediol. The diol could then be oxidized to the desired dipivaloylmethane. The reaction sequence is illustrated in Figure 3.

The first step in the synthesis involved the selective oxidation of 1,3-propanediol to malonaldehyde. Attempts to effect this oxidation by common (5,6,7) procedures did not give malonaldehyde in any significant yield. Several oxidation systems were designed and tested for the preparation of malonaldehyde from 1,3-propanediol and the most efficient version is shown in Figures 4, 5, 6, and 7. The system consisted of a boiling flask, a metal reaction chamber, and a fractional distillation assembly.

A. Metal Reaction Chamber: The metal reaction chamber was designed with the following specifications:

A one-foot section of $2\frac{1}{2}$" galvanized water pipe was threaded at each end and fitted with regular screw-on caps. The threads were covered with teflon tape (Strip-Teeze) to minimize leakage. Two inlet tubes, sealed at the end, were welded into one of the caps to accommodate the leads of a thermostat and thermocouple system. The chamber had its inlet, outlet and return connections made of $\frac{1}{4}$" stainless

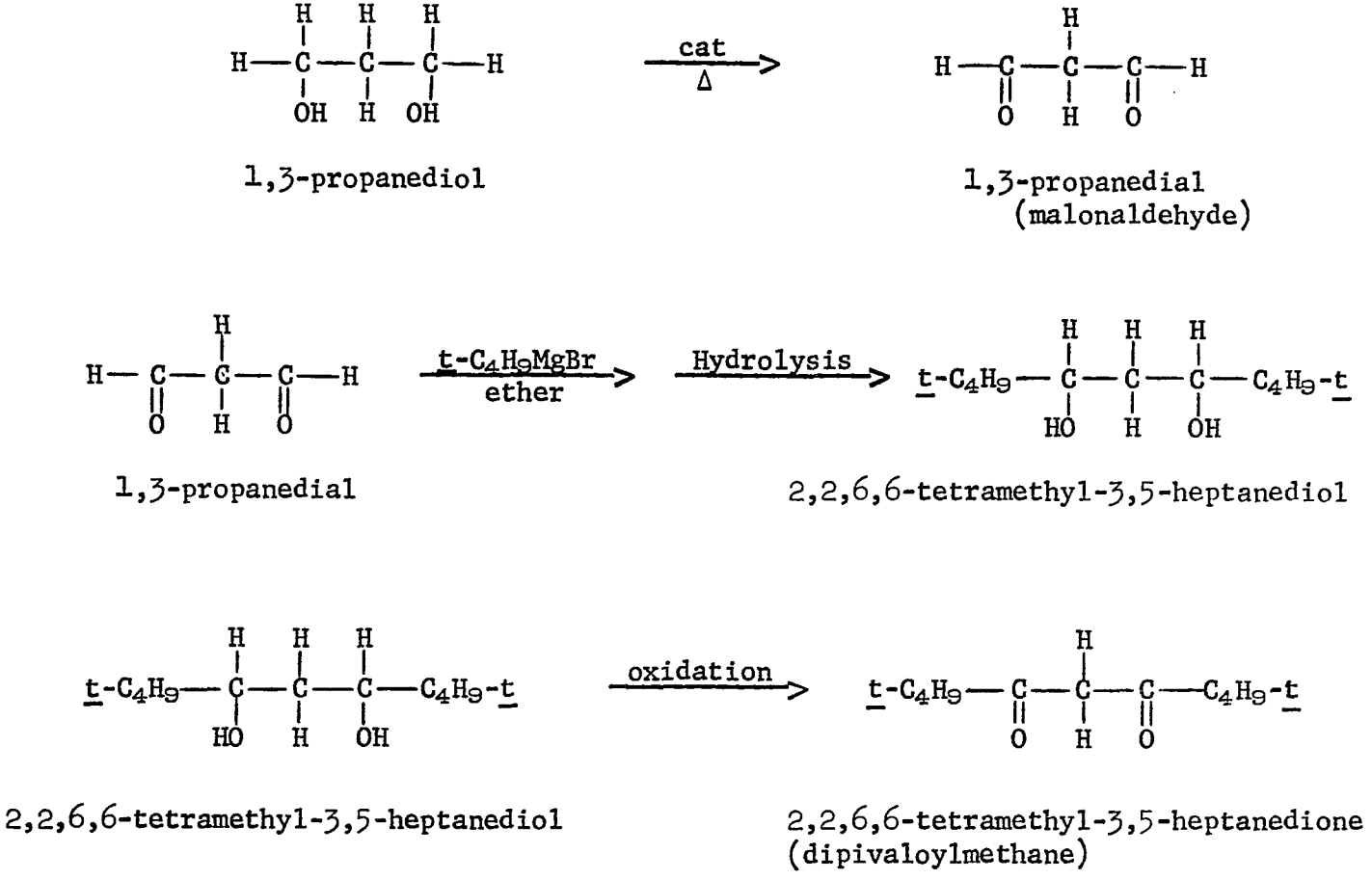


FIGURE 3. Proposed Synthesis of Dipivaloylmethane

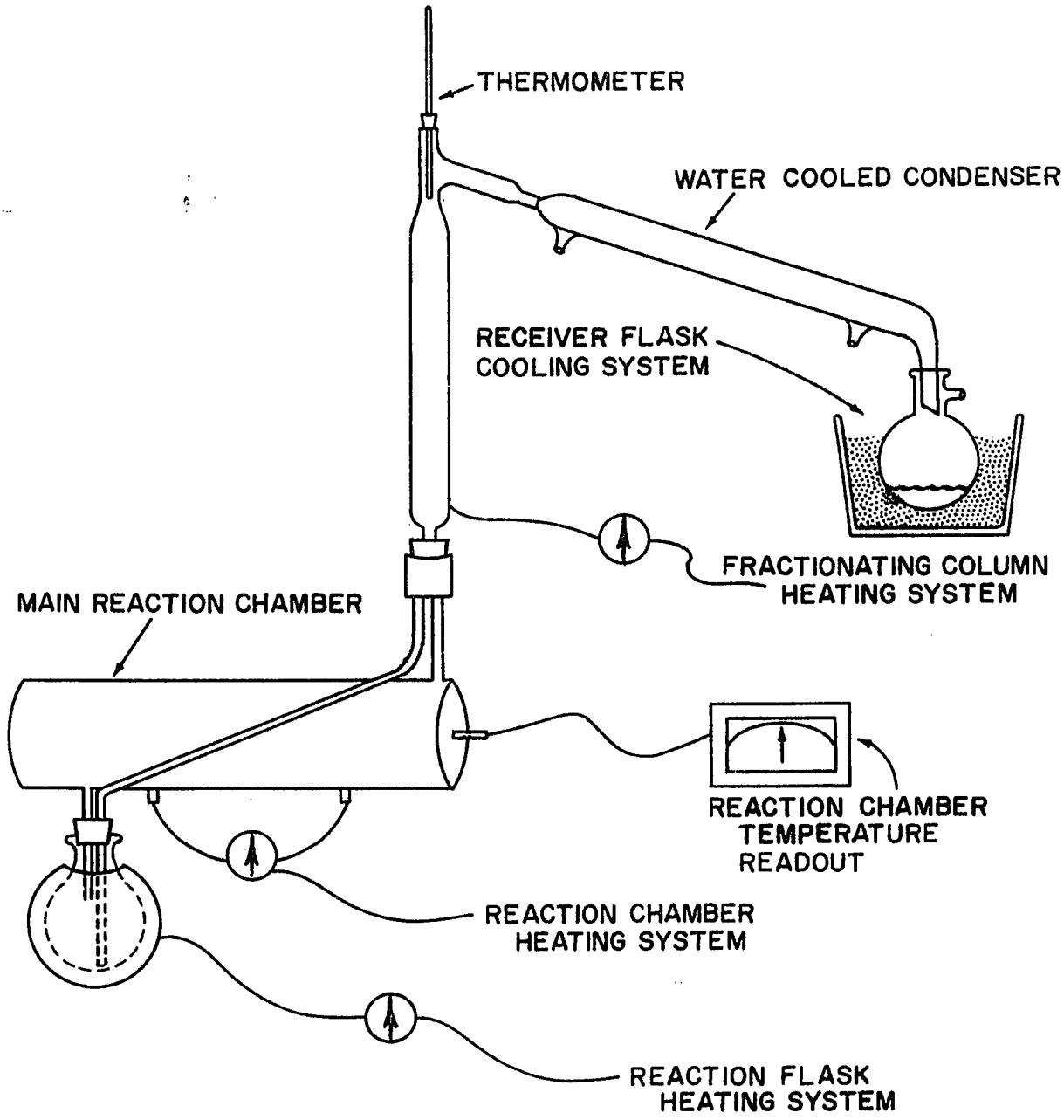
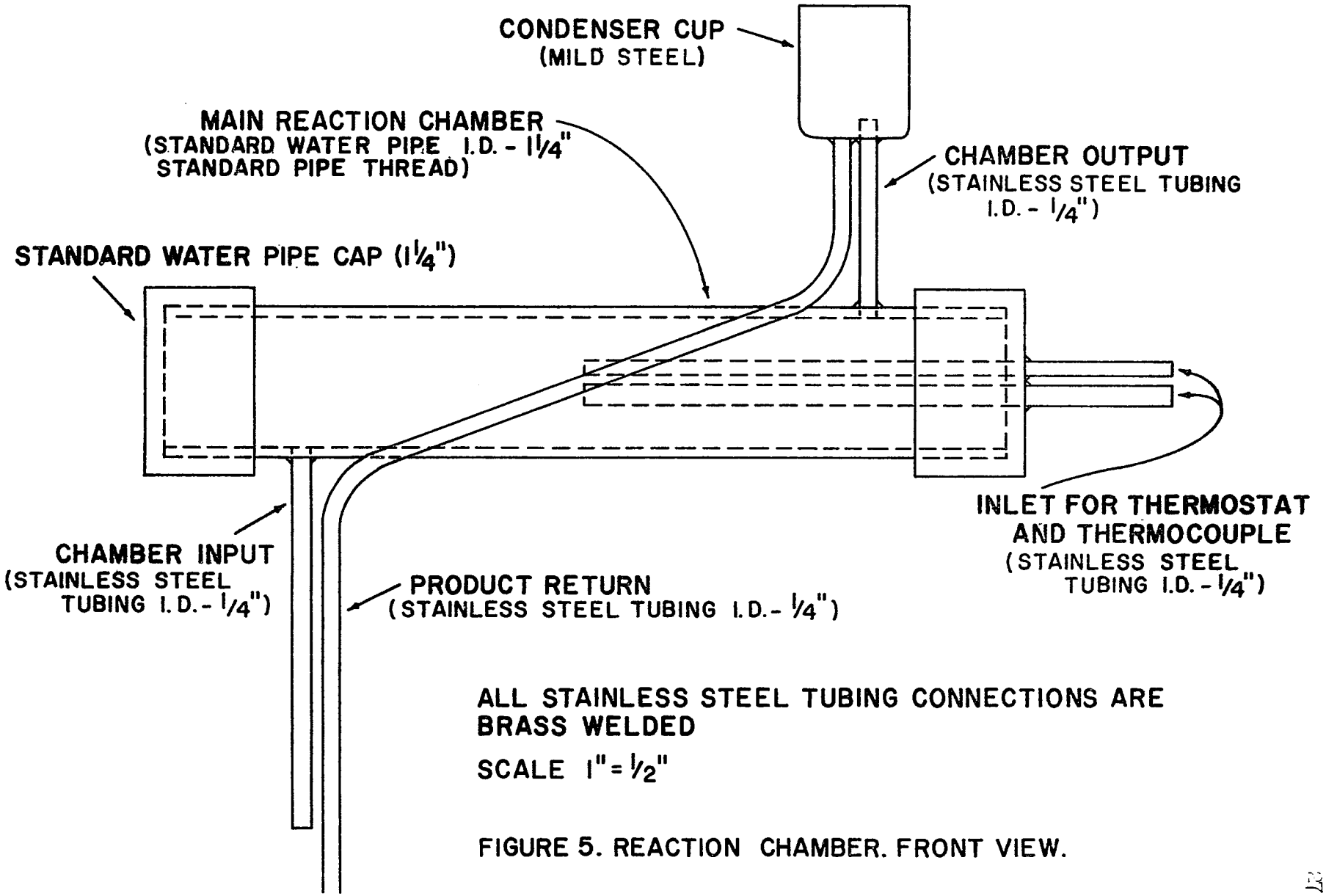


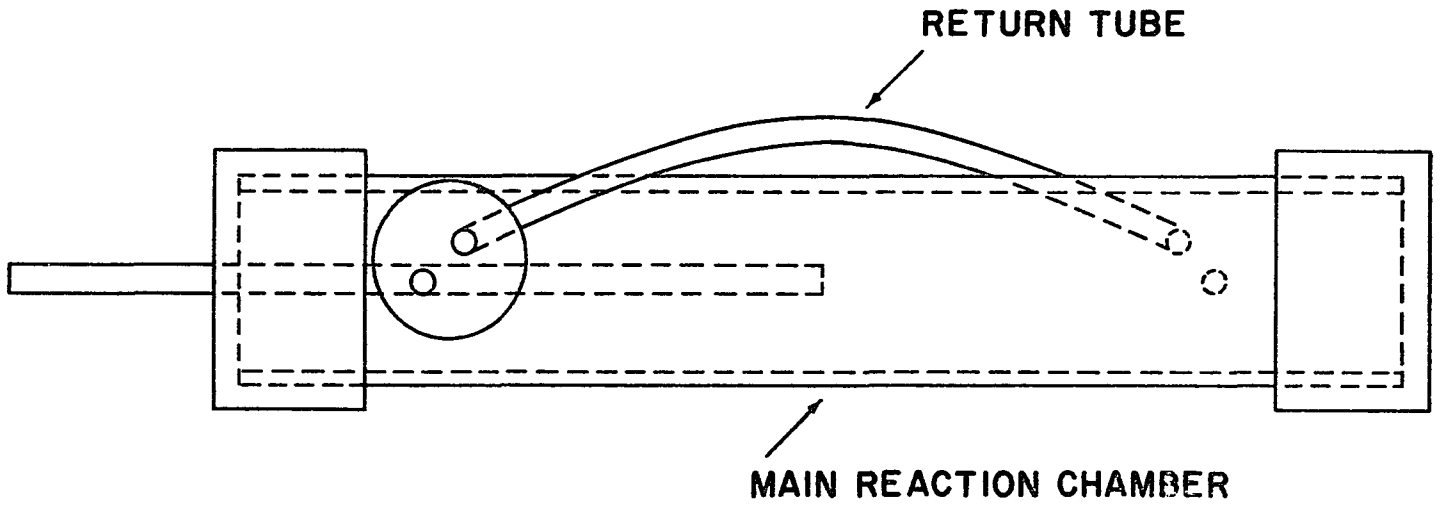
FIGURE 4. SKETCH OF THE SYSTEM USED FOR THE OXIDATION OF ALCOHOLS



ALL STAINLESS STEEL TUBING CONNECTIONS ARE BRASS WELDED

SCALE 1" = ½"

FIGURE 5. REACTION CHAMBER. FRONT VIEW.



SCALE 1" = 1/2"

FIGURE 6. REACTION CHAMBER. TOP VIEW.

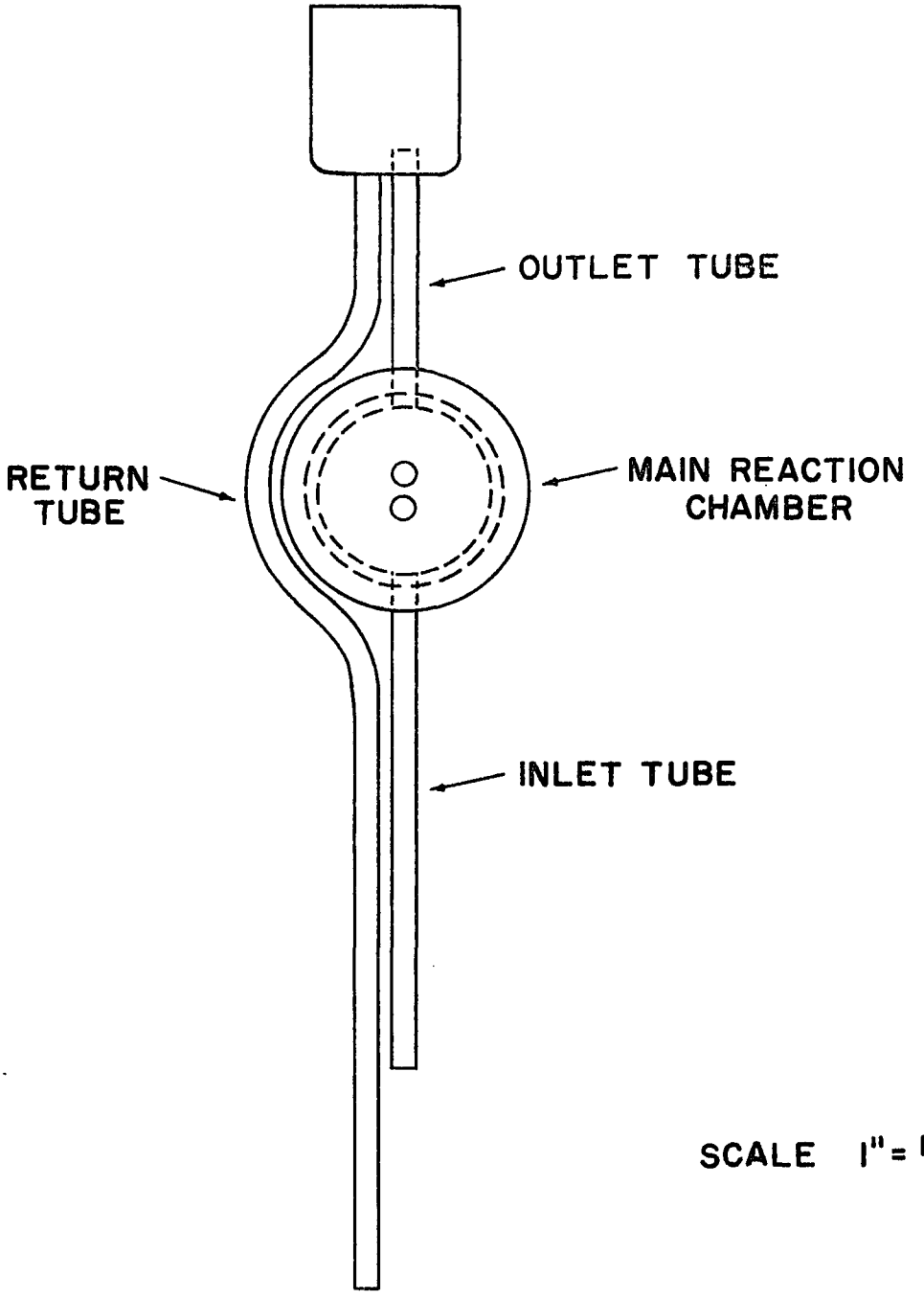


FIGURE 7. REACTION CHAMBER. SIDE VIEW.

steel tubing. Additional construction details can be seen in Figures 5, 6, and 7. The chamber was heated with a heating element directly wound around the pipe and connected to a powerstat. The temperature readout consisted of an iron-constantine thermocouple connected to a calibrated meter. The whole chamber assembly was covered by several layers of glass wool tape to prevent heat losses. The upper part of the chamber incorporated a mild steel cup which provided a connection to the fractional distillation system.

B. Oxidation Procedure: The alcohol was placed in a round bottom flask under the reaction chamber and the flask was heated to a temperature slightly above the boiling point of the liquid. The vapors flowed into the reaction chamber where they made contact with the reagent or catalyst which was dispersed between layers of glass wool and then flowed into the fractional distillation assembly. The higher boiling components were returned to the reaction flask for recycling and the lower boiling components were recovered in an ice-salt cooled system. The temperature of the fractionating column was kept hot enough to allow a slow, continuous distillation rate. The reaction chamber was tested using temperatures which ranged from 200 to 700°C. The temperature ranges used in the individual experiments can be seen in Table VIII.

C. Reactant and Catalysts: The efficiency of various oxidation reactants or catalysts in the system was tested by using three different substances in the reaction chamber. These substances were: copper turnings, copper oxide wire and a copper-chromium oxide catalyst (49). The literature (5,6,7,26) makes reference to many

TABLE VIII

Data On the Oxidation of Alcohols

Experiment Number	Reagent or Catalyst	Chamber Temperature °C	Aldehyde in Product %	Total Aldehyde Yield %
		BENZYL ALCOHOL		
1	CuO[a]	325-375	43	27
2	CuO	310-330	54	41
3	CuO	290-310	53	39
4	Cu-chrom[b]	312-330	70	31
5	Cu-chrom	230-250	54	41
6	Cu[c]	650-670	NR[d]	NR
7	Cu	300-330	NR	NR
8	Cu + air	300-330	NR	NR
9	Cu + air	600-620	NR	NR
		CYCLOHEXANOL		
1	CuO	300-320	75	45
2	CuO	400-420	67	40
3	Cu-chrom	300-320	80	44
4	Cu-chrom	350-370	40	14[e]
5	Cu	300-320	NR	NR
6	Cu + air	300-325	NR	NR
		1-HEPTANOL		
1	CuO	310-320	58	45
2	Cu-chrom	310-325	55	40
3	Cu	310-325	NR	NR
		1,3-PROPANEDIOL		
1	CuO	290-310	20	16
2	CuO	270-280	32	26
3	CuO	270-280	30	21

a. Copper oxide wire.
b. Copper-chromium oxide catalyst (49).
c. Copper turnings.
d. Leaks developed in the system.

compounds used for the oxidation of alcohols but they are usually noble metals or mixed chemicals type catalysts. These catalysts are generally expensive or difficult to make, while copper oxide wire is a cheap readily available reactant.

2. Preliminary Reactions: The efficiency of the oxidation system was tested by the oxidation of benzyl alcohol, cyclohexanol and 1-heptanol. These alcohols were chosen because their study would provide data on different types of products which could be used to evaluate the system in terms of per cent recovery, per cent yield and mechanism of reaction. The results of these experiments are shown in Table VIII.

The qualitative evaluation of the reaction products was done by the mixed chromatogram technique in a Beckman GC-5 (Carbowax 20M) and in a Glowal 320 (15% SE 30) instrument. Quantitative evaluations were done on a Varian Aerograph Model 90 instrument. Peak areas were calculated by multiplying the peak height at the maximum by the peak width at half height (50). Calibration curves were prepared by using reagent grade chemicals.

A. Reaction of Benzyl Alcohol: The main organic products of this reaction were benzene, benzaldehyde and toluene. These gas phase reactions probably took place through free radical mechanisms, surface catalysis or both (51,52). The amount of benzene produced was less than 5% of the total product and its origin could be attributed to the decarbonylation of benzaldehyde (6, 53, 54). Toluene recovery in the product varied between 25 and 60% and its origin could be attributed to the hydrogenolysis (6,55) of benzyl alcohol. Benzaldehyde recovery

in the product varied between 40 and 70% and its origin could be attributed to the oxidation of benzyl alcohol (5,6,7).

B. Reaction of Cyclohexanol: The main organic products of the reaction of cyclohexanol were cyclohexanone and cyclohexene. Cyclohexene recovery in the product varied between 20 and 60% and its origin could be attributed to the dehydration of cyclohexanol (5,6,7). Cyclohexanone per cent varied between 40 and 80% and its origin could be attributed to the oxidation of cyclohexanol (5,6,7).

C. Reaction of 1-Heptanol Alcohol: The main organic products of this reaction were heptaldehyde and 1-heptene. The mixture contained many low boiling components of which only 2-heptene and heptane could be identified. The recovery of heptaldehyde averaged around 43%, but it was present in such a complex mixture that its purification was impossible. The origin of the heptaldehyde could be attributed to the oxidation of 1-heptanol (5,6,7). The origin of the other components was probably due to cracking and dehydration during the reaction (27,51,52).

3. Reaction of 1,3-Propanediol

The main organic products of the reaction of 1,3-propanediol were malonaldehyde and acrolein. The presence of malonaldehyde was colorimetrically determined by the use of four different reagents [methods A, B, D, and E of Sawicki (56)] and by gas chromatography. The mixture also contained many low boiling compounds among which only the following could be identified: formaldehyde, acetaldehyde and

propionaldehyde. The product recovery averaged from 20% to 35%. The origin of acrolein could be attributed to the dehydration of the diol (5,6,7). Recovery of this component in the product ranged from 35 to 50%. The quantitative evaluation of malonaldehyde had to be done by using the method suggested by Kwon (57), because it was not possible to prepare a reliable calibration curve to use with the chromatographic data.

The following procedure is an adaptation of the method suggested by Kwon (57) for mixtures of this type:

An aliquot portion of the sample mixture was treated with deionized water, and the aqueous layer was separated from the organic layer in a separatory funnel and then filtered. The resulting clear aqueous solution was diluted by trial and error to a concentration suitable for analysis (57). Two 10-ml portions of the solution were adjusted to pH 11.3 and 2.3 by the addition of 0.1 ml of 1N aqueous solution of sodium hydroxide and hydrochloric acid respectively. The absorbance of the acidic and basic solutions were read against each other in a 1 cm cell at 267 nm. The concentration was then interpolated from a standard curve prepared by hydrolyzing 1,1,3,3-tetramethoxy-propane with dilute hydrochloric acid (57). The results of this work are shown in Table VIII, and the calibration curve is shown in Figure 8.

V. Fractional Sublimation of β-Dicarbonyl Metal Chelates.

The study of the volatility and separability of metal chelates by fractional sublimation was done either on a Berg sublimator or in the larger version of the sublimator which was designed by the author

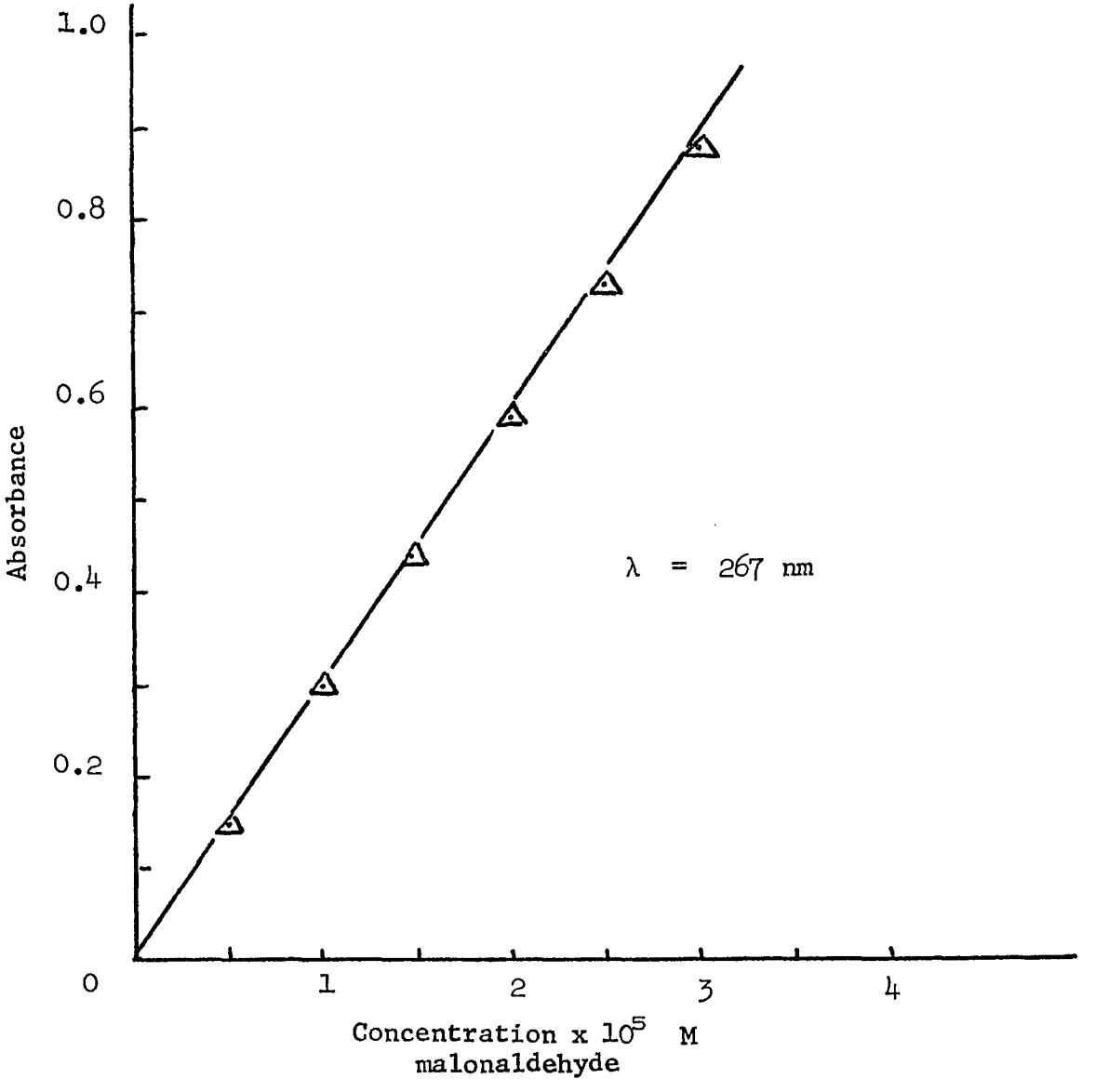


FIGURE 8. Calibration Curve for the Quantitative Determination of Malonaldehyde

(Figure 2). All individual sublimation-condensation temperature zones were studied in the small sublimator. The qualitative and quantitative evaluation of synthetic mixture was done in the small sublimator except for the mixtures of beryllium and copper-dipivaloylmethane chelates, which were also done in the large sublimator.

1. The Effects of Experimental Parameters on the Sublimation-Condensation Temperature Zone.

A. Temperature Gradient: Before the other experimental parameters were studied it was necessary to determine the temperature gradient, of each sublimator, at selected powerstat settings. These temperature gradients are shown in Figures 9 and 10. Once the temperature gradient-voltage relationships had been established for a given system, the temperature readings were reproducible within $\pm 2^{\circ}C$.

B. Best Sublimation Conditions: The following parameters were varied in order to determine the optimum conditions for obtaining discrete condensation zones: powerstat setting (temperature), air pressure, total pump time, total heating time, relationship between pump time and heating time, and the temperature of the glass tube when extracted from the sublimator. Typical results from this investigation are shown in Table IX and Figure 11. The solid lines in Figure 10 represent the main condensation zones where crystals can be easily observed by the naked eye. The dotted lines represent the zones of diffuse condensation where crystals are visible under magnification higher than 10X.

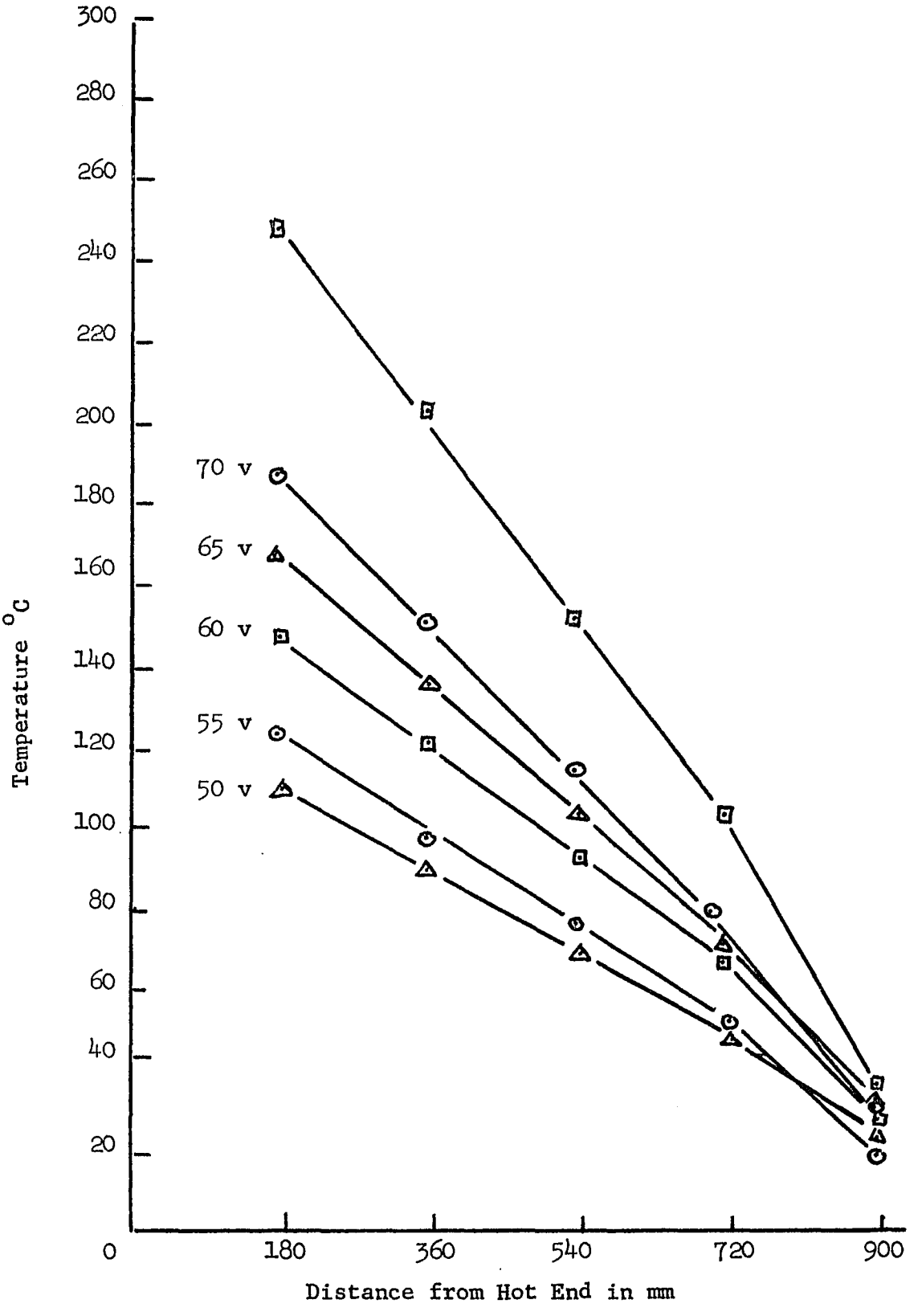


FIGURE 9: Temperature Gradient-Voltage Data for the Small Sublimator

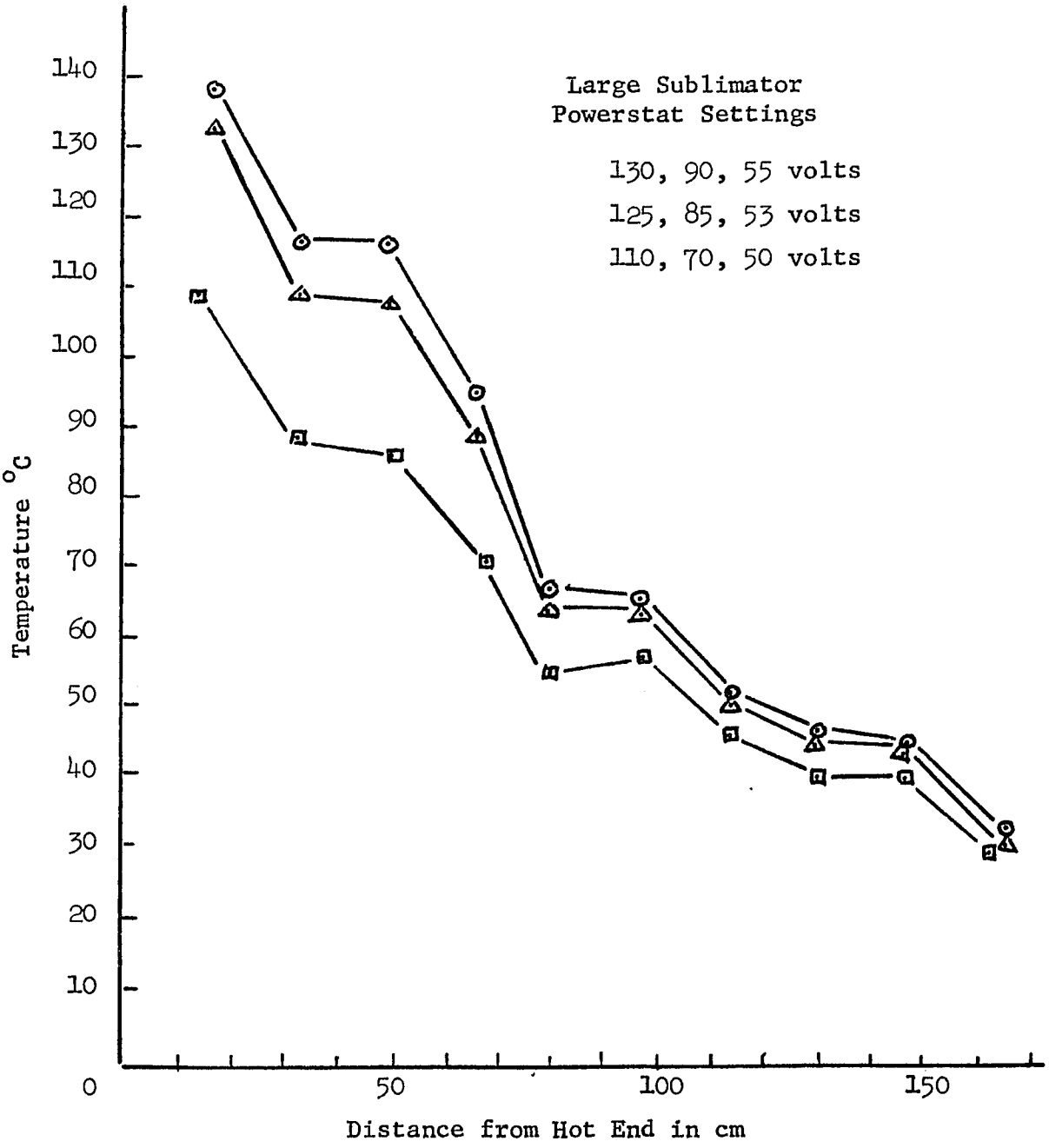


FIGURE 10. Temperature Gradient-Voltage Data for the Large Sublimator

TABLE IX

DATA ON SUBLIMATION PARAMETERS

Chelate	Run No.[a]	Pump Time	Voltage	Air Press.	Other Parameters
$Al(DPM)_3$	1	105 min.	55 v	1 mm	Sublimator tube: cold. Heat off: 60 min. Pump off: 105 min. Glass tube out: cold.
$Al(DPM)_3$	2	60 min.	55 v	1 mm	Sublimator tube: cold. Heat & Pump off: 60 min. Glass tube out: cold.
$Al(DPM)_3$	3	60 min.	55 v	0.5 mm	Sublimator tube: cold. Heat & Pump off: 60 min. Glass tube out: cold.
$Al(CPM)_3$	4	120 min.	55 v	0.5 mm	Sublimator tube: cold. Heat & Pump off: 120 min. Heat off 15.5 hr. Glass tube out: cold.
$Al(DPM)_3$[b]	5	60 min.	65 v	0.5 mm	Sublimator tube: preheated. Pump off: 60 min. Glass tube out: hot.
$Al(DPM)_3$	6	60 min.	90 v	0.5 mm	Sublimator tube: preheated. Pump off: 60 min. Glass tube out: hot.
$Al(CPM)_3$	7	60 min.	70 v	0.5 mm	Sublimator tube: preheated, Pump off: 60 min. Glass tube out: hot.
$Cu(DPM)_2$	1	90 min.	90 v	1 mm	Sublimator tube: cold. Heat off: 60 min. Pump off: 90 min. Glass tube out: cold.
$Cu(DPM)_2$	2	120 min.	55 v	1.1 mm	Sublimator tube: cold. Heat off: 80 min. Pump off: 120 min. Glass tube out: cold.
$Cu(DPM)_2$	3	85 min.	55 v	0.5 mm	Sublimator tube: preheated. Pump off: 85 min. Glass tube out: hot.
$Cu(DPM)_2$	4	120 min.	65 v	0.5 mm	Sublimator tube: preheated. Pump off: 120 min. Glass tube out: hot.
$Cu(DPM)_2$[b]	5	60 min.	65 v	0.5 mm	Sublimator tube: preheated. Pump off: 60 min. Glass tube out: hot.
$Fe(CPM)_3$	1	60 min.	65 v	0.5 mm	Boat out: 20 min. Sublimator tube: preheated. Pump & heat: 60 min. Glass tube out: cold.

TABLE IX (cont'd)

Chelate	Run No.[a]	Pump Time	Voltage	Air Press.	Other Parameters
$Fe(DPM)_3$	2	60 min.	55 v	0.5 mm	Sublimator tube: cold. Pump & heat: 60 min. Glass tube out: cold.
$Fe(DPM)_3$	3	60 min.	55 v	0.5 mm	Sublimator tube: preheated. Pump off: 60 min. Glass tube out: hot.
$Fe(DPM)_3$	4	60 min.	55 v	0.5 mm	Boat out: 30 min. Sublimator tube: preheated. Pump off: 60 min. Glass tube out: hot.
$Fe(DPM)_3$[b]	5	60 min.	65 v	0.5 mm	Sublimator tube: preheated. Pump off: 60 min. Glass tube out: hot.

[a]These designations correspond to those found in Figure 11.

[b]Best sublimation conditions.

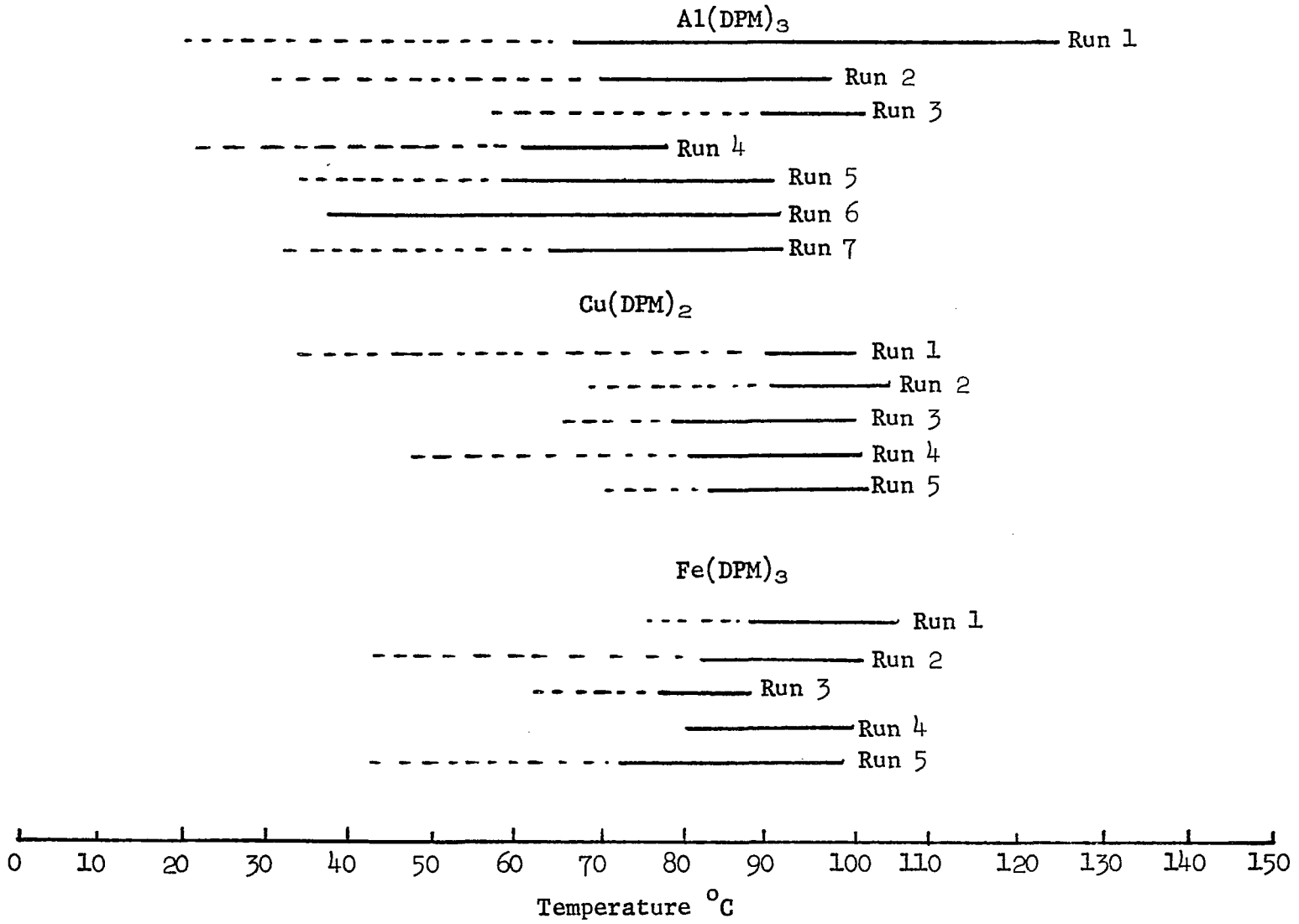


FIGURE 11. Relationship Between Condensation Zone and Sublimation Parameters

From the available information it was decided that the best defined and shortest temperature condensation zones were obtained by using the following parameters:

Pump operation time: 60 minutes

Air Pressure: 0.5 mm of mercury

Setting-Powerstat no. 1: 65 volts

Condenser system: ice cooled

Sublimation glass tube: removed hot

The detailed sublimation procedure used for determining individual sublimation condensation temperature zones was as follows: The sublimator system, including the sublimation glass tube, was preheated to the maximum temperature corresponding to the selected powerstat setting. The pump was turned on, and the system was regulated to the desired air pressure. The pump was allowed to run the desired time and then was isolated from the system, without breaking the vacuum. The system was then allowed to bleed, through the air pressure regulator, until the system reached equilibrium with the outside pressure. The glass tube then was removed hot and capped until it was evaluated.

2. Individual Sublimation-Condensation Temperature Zones

The individual sublimation-condensation temperature zones for the volatile β-carbonyl metal chelates analyzed in this study are shown in Figures 12, 13, and 14. The solid lines in these figures represent the main condensation zones where crystals can be easily

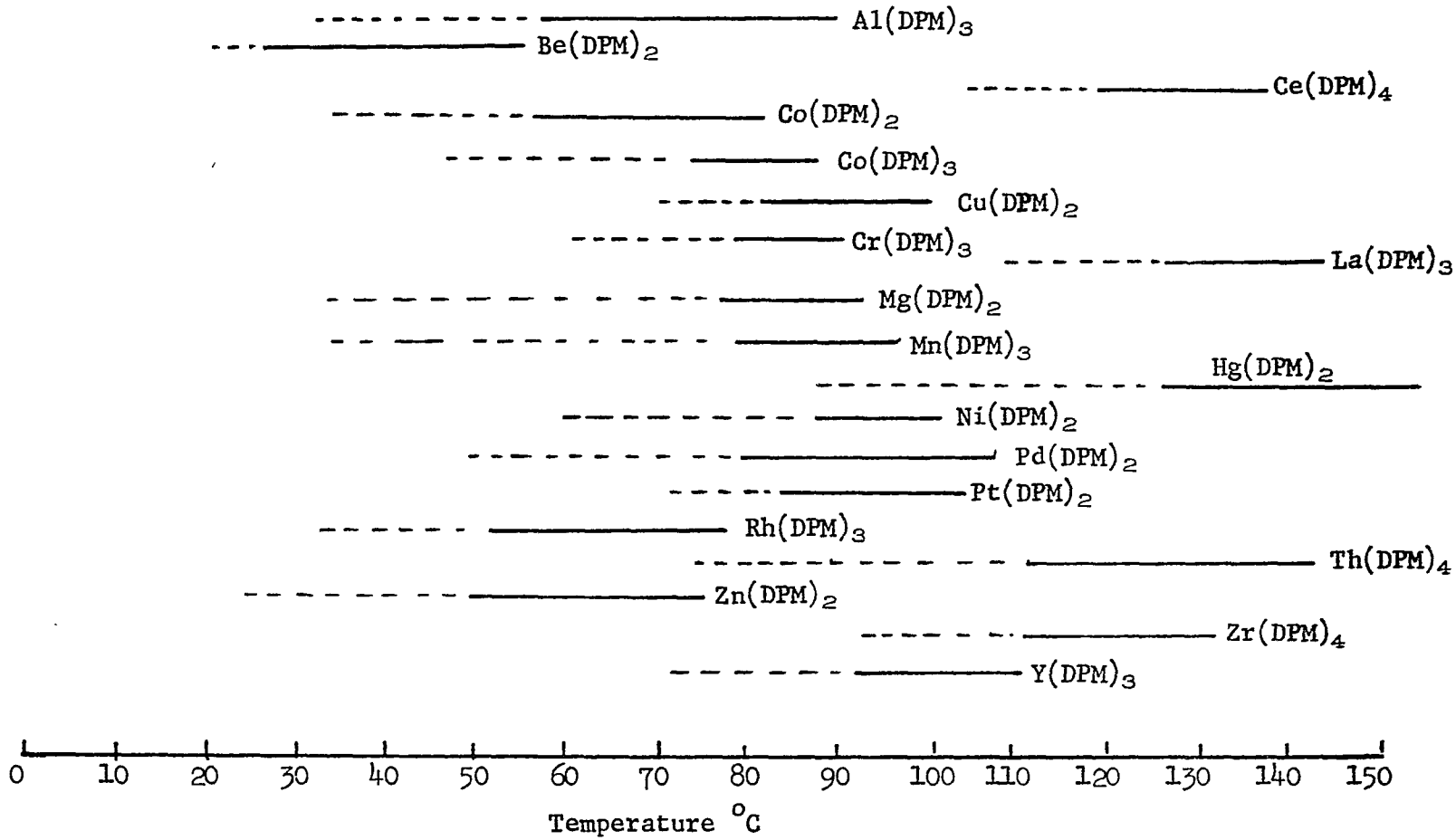


FIGURE 12. Individual Sublimation-Condensation Temperature Zones for the Metal Chelates of Dipivaloylmethane

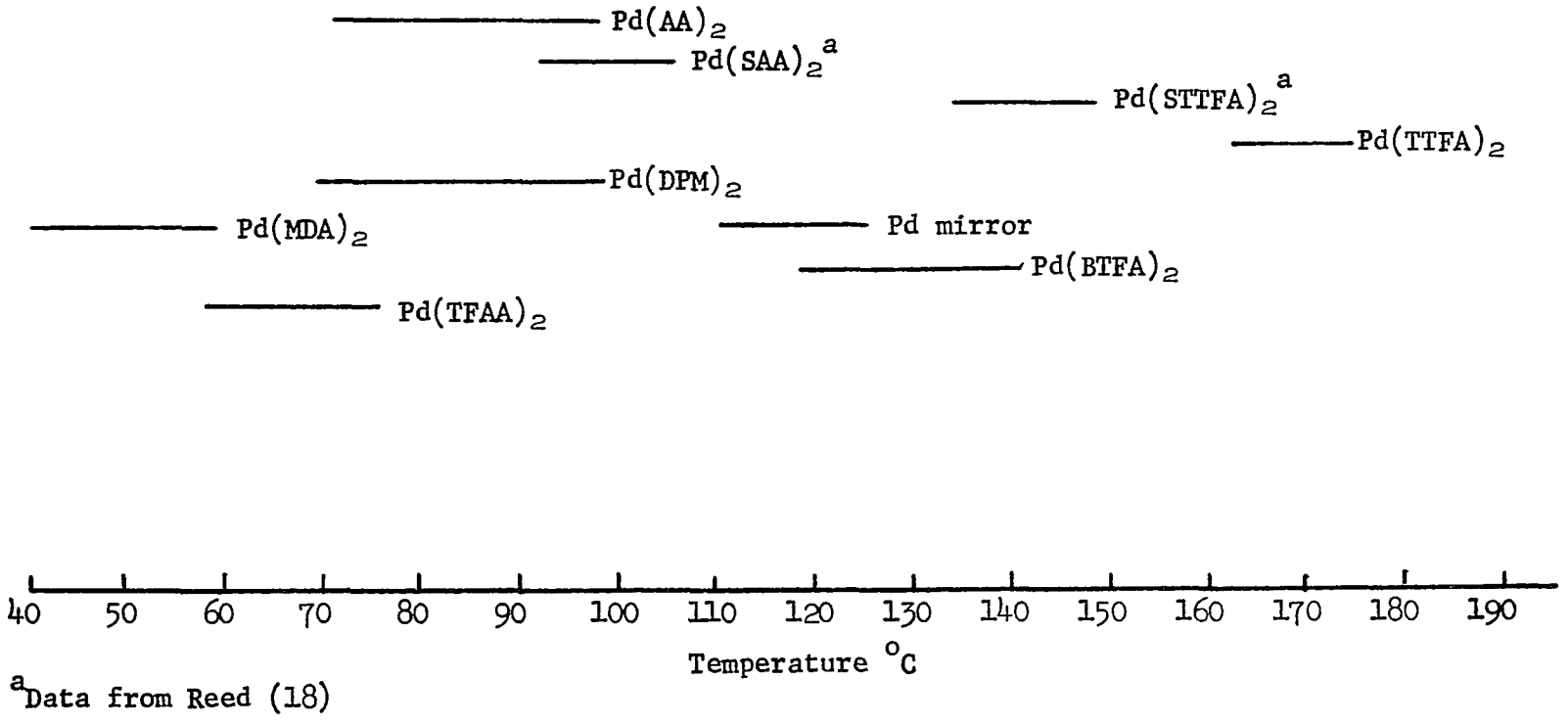
observed by the naked eye. The dotted lines represent the zones of diffuse condensation where crystals are visible under magnification higher than 10X.

The dipivaloylmethane chelates of calcium (II), strontium (II), barium (II), and cadmium (II) are not shown in Figure 11 because they were found to be non-volatile under the experimental conditions previously outlined.

The condensation temperature zones of palladium and chromium, tied to different β-dicarbonyl ligands, are shown in Figures 13 and 14.

3. Separation of Metal Chelate Mixtures of Dipivaloylmethane by Fractional Sublimation.

A. Modification of the Fractional Sublimation Procedure for Mixtures: After the fractional sublimation study for individual chelates was completed, Dr. K. Reed, in a seminar at Louisiana State University-Baton Rouge, indicated that he had made some condensation temperature zones shorter by introducing a glass wool plug between his sample and the air pressure regulator. Dr. A. Shendrikar then indicated that he had not observed such a phenomenon during his fractional sublimation studies. To resolve this discrepancy the author decided to study the effects of placing glass wool plugs at selected intervals in the glass tube. Glass wool plugs were placed in front of the sample boat (pump side), behind the sample boat, and in the condenser region, and the effects on the separation of mixtures were studied. The results are summarized in Figure 15.



[a]Data from Reed (18)

FIGURE 13. Individual Sublimation-Condensation Temperature Zones for β-Dicarbonyl Chelates of Palladium (II)

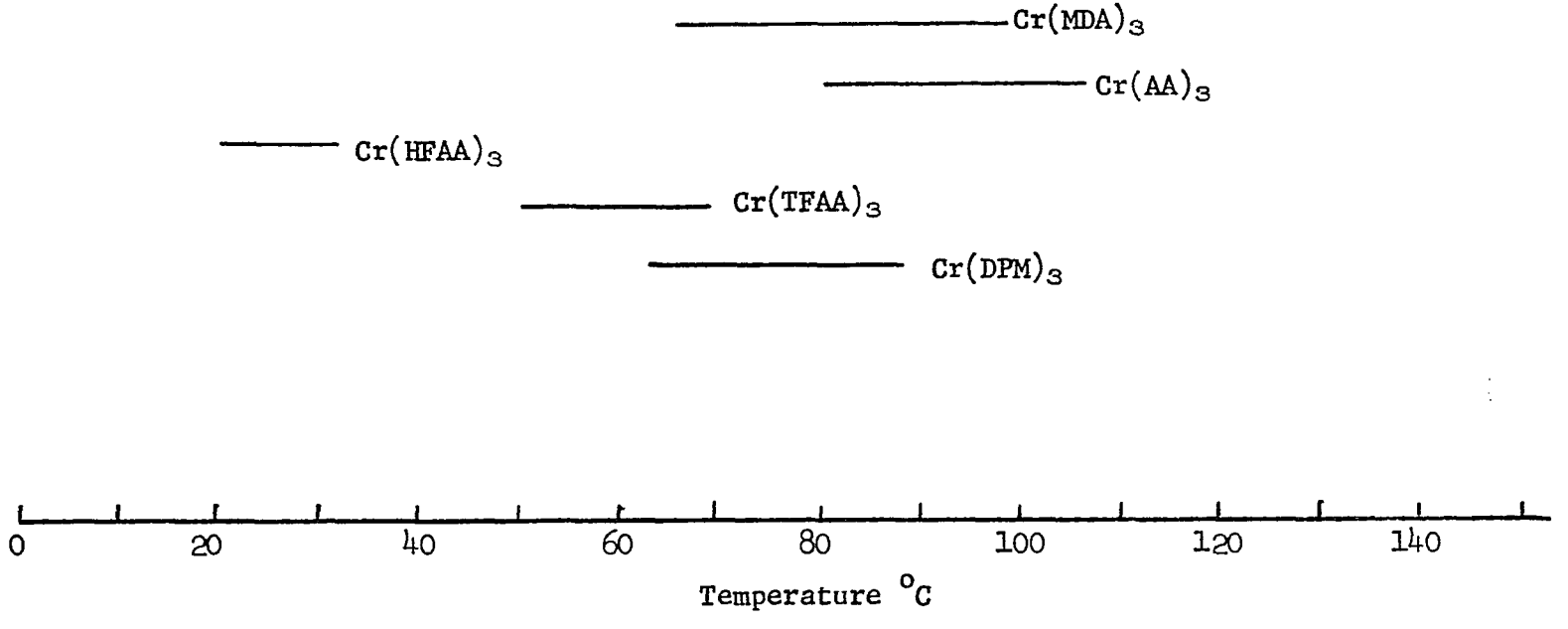


FIGURE 14. Individual Sublimation-Condensation Temperature Zones for β-Dicarbonyl Chelates of Chromium (III).

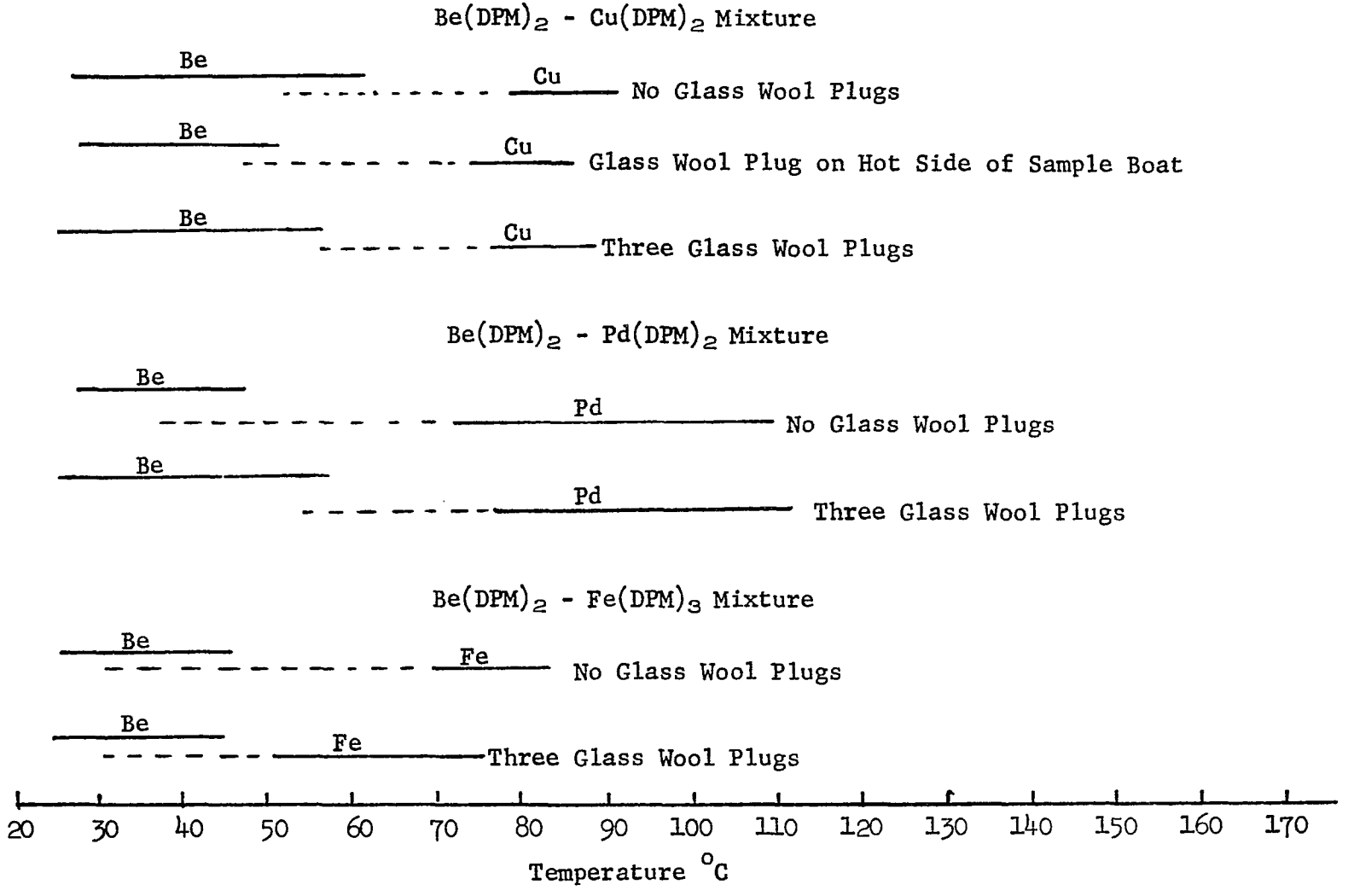


FIGURE 15. Effects of Glass Wool Plugs on the Fractional Sublimation of Mixtures of Dipivaloylmethane Metal Chelates

B. Fractional Sublimation of Binary and Ternary Synthetic Mixtures of Volatile Metal Chelates of Dipivaloylmethane: The fractional sublimation of mixtures was done by introducing the three glass wool plugs, mentioned in the previous section, into the sublimation system because it was found that it would improve separation. The results of these fractional sublimations of mixtures are shown in Figures 16, 17, and 18. Two binary mixtures were studied by this method using the large sublimator, and the results are shown in Figure 17.

The binary mixtures shown in Figure 17 and the two shown in Figure 18 were evaluated quantitatively and the results are discussed in the next section.

C. Analytical Methods Used in the Quantitative Evaluation Of the Separability of Metal Chelates by Fractional Sublimation: Hartlage (16) and Chiang (17) proved that data on individual sublimation-condensation temperature zones provide an accurate guideline for the prediction of separability of synthetic mixtures of the same compounds. Their work (16,17) provides qualitative and quantitative data which indicate that the high temperature end of a given sublimation-condensation temperature zone is always sharp.

To complement the qualitative study, it was decided to evaluate quantitatively the degree of separation achieved by fractional sublimation in mixtures of the dipivaloylmethane chelates of beryllium and copper; rhodium and platinum; and rhodium and palladium. The results of this study are shown in Tables X, XI, and XII.

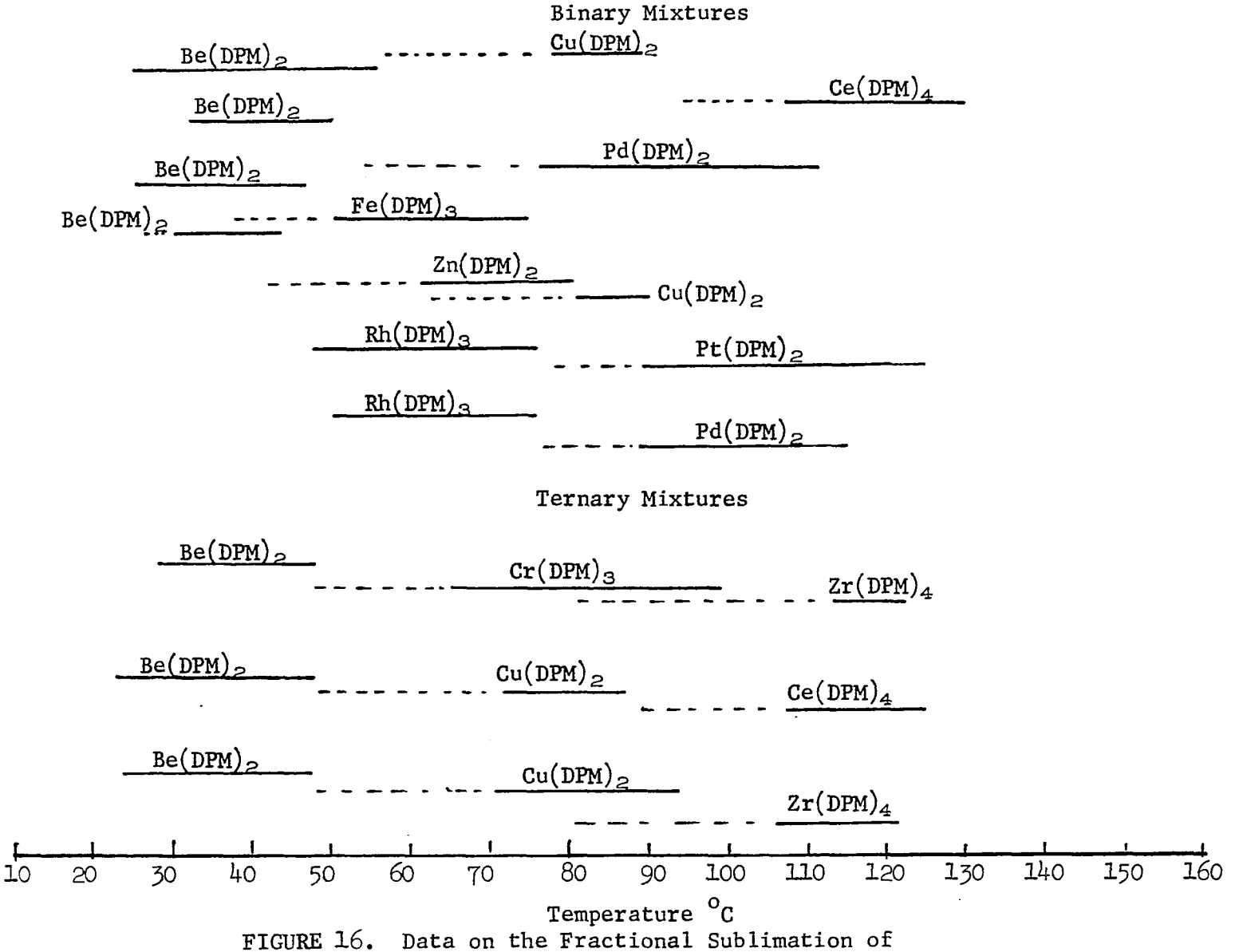
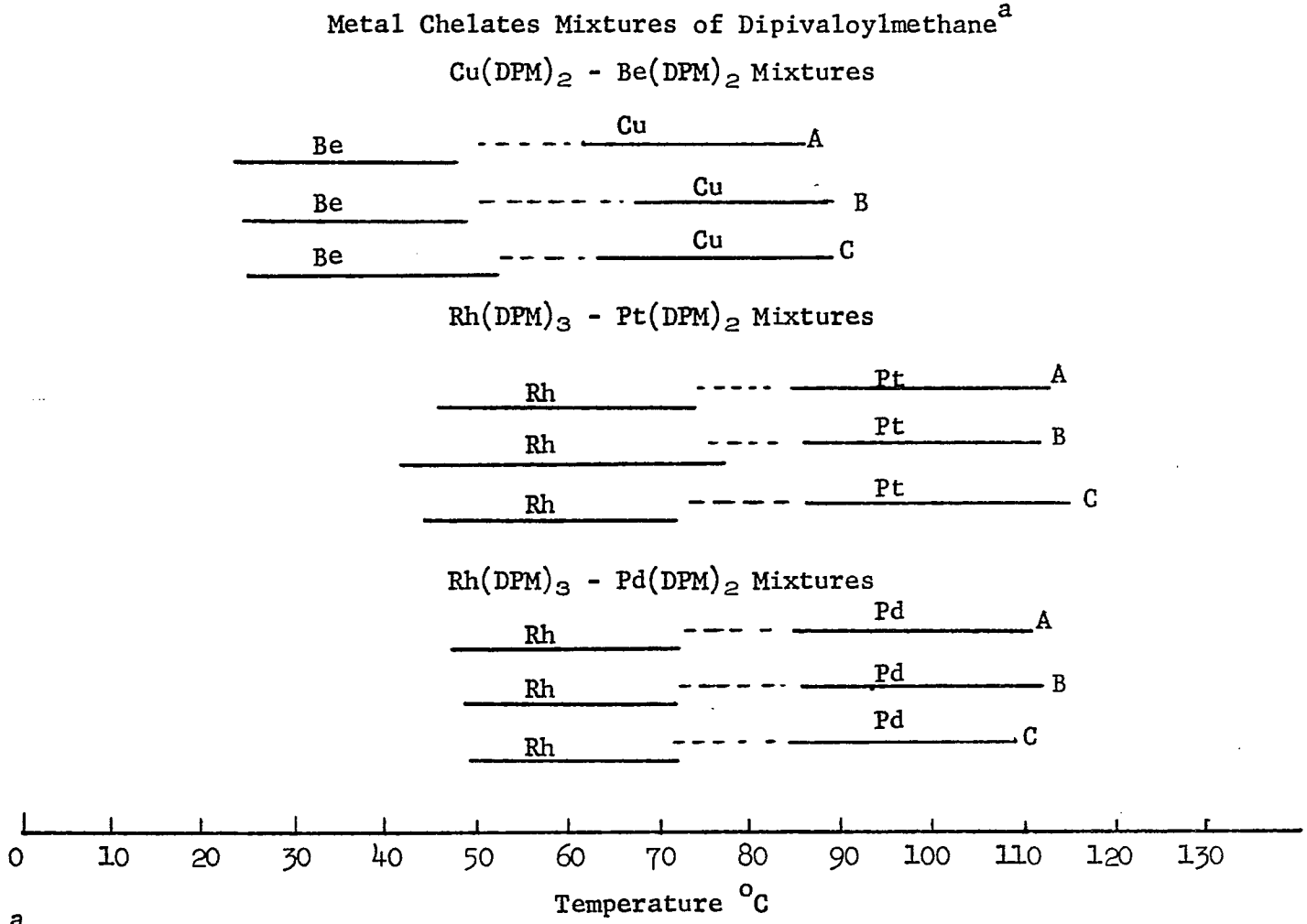


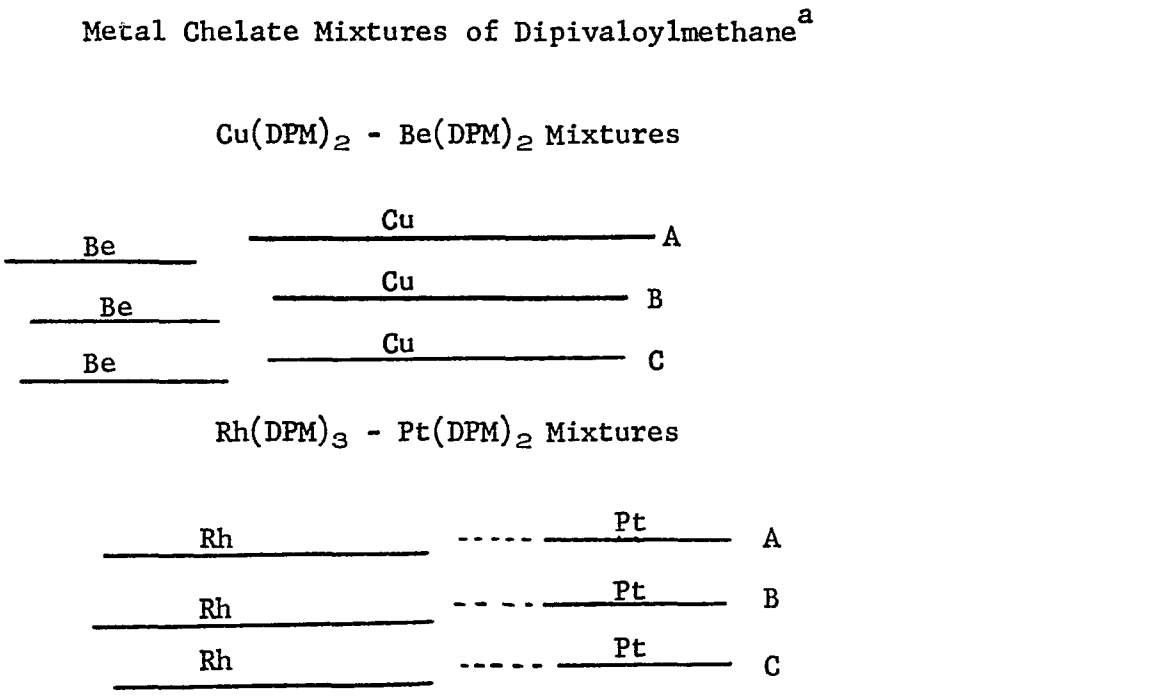
FIGURE 16. Data on the Fractional Sublimation of Metal Chelate Mixtures in the Small Sublimator



[a]Quantitative Evaluations are shown in Tables X, XI, XII

FIGURE 17. Data on the Fractional Sublimation of Mixtures of Metal Chelates Evaluated Quantitatively (Small Sublimator)

Metal Chelate Mixtures of Dipivaloylmethane[a]



[a]Quantitative Evaluations are shown in Tables XIII and XIV

FIGURE 18. Data on the Fractional Sublimation of Mixtures of Metal Chelates Evaluated Quantitatively (Large Sublimator)

TABLE X

QUANTITATIVE EVALUATION OF THE COPPER CONTENT IN $Cu(DPM)_2$-$Be(DPM)_2$ MIXTURES SEPARATED BY FRACTIONAL SUBLIMATION[a]

Experiment Designation[b]	Original Copper Content mg.	Copper in Copper Rich Zone mg.	Copper in Beryllium Rich Zone mg.
A	1.05	1.01	0.03
B	0.96	0.95	0.01
C	1.26	1.26	0.00

[a]Small sublimator.

[b]These designations correspond to those found in Figure 17.

TABLE XI

QUANTITATIVE EVALUATION OF THE RHODIUM CONTENT IN $Rh(DPM)_3$-$Pt(DPM)_2$ MIXTURES SEPARATED BY FRACTIONAL SUBLIMATION[a]

Experiment Designation[b]	Original Rhodium Content mg.	Rhodium in Rhodium Rich Zone mg.	Rhodium in Platinum Rich Zone mg.
A	1.12	1.12	0.00
B	0.79	0.78	0.00
C	0.99	0.98	0.00

[a]Small sublimator

[b]These designations correspond to those found in Figure 17.

TABLE XII

QUANTITATIVE EVALUATION OF THE RHODIUM CONTENT IN $Rh(DPM)_3$-$Pd(DPM)_2$ MIXTURES SEPARATED BY FRACTIONAL SUBLIMATION[a]

Experiment Designation[b]	Original Rhodium Content mg.	Rhodium in Rhodium Rich Zone mg.	Rhodium in Palladium Rich Zone mg.
A	0.96	0.96	0.00
B	0.79	0.77	0.00
C	0.74	0.74	0.00

[a] Small sublimator

[b] These designations correspond to those found in Figure 17.

Mixtures of the dipivaloylmethane chelates of beryllium and copper andof rhodium and platinum were separately sublimed in the large sublimator and evaluated quantitatively. The results of this study are shown in Tables XIII and XIV.

a. Copper Analysis: The amount of copper recovered during sublimation was determined by using the diethyldithiocarbamate method described by Sandell (2). The procedure used was identical to that suggested by Sandell except for minor modifications which are outlined in the following description: The sublimation tube was removed hot, capped and allowed to cool to room temperature. The tube was then cut at the intervals selected for study and carefully washed with a total of 50 ml of 1N hydrochloric acid solution. The solution was heated, if necessary, to insure complete dissolution and then an aliquot was diluted to the appropriate concentration (2) using deionized, distilled water. A 15 ml sample of the final solution contained 1.0×10^{-6} to 20.0×10^{-6} g of copper. The solution was then buffered with 5 ml of a 20% aqueous solution of ammonium citrate and the pH was adjusted to 9.0 by adding 6N aqueous ammonia. The basic solution was then placed in a separatory funnel, 5.0 ml of Spectrograde carbon tetrachloride along with 1.0 ml of a 0.1315% N,N-sodium diethyldithiocarbamate solution was added, and the mixture was shaken for 2 minutes. The liquids were allowed to reach equilibrium for 2 minutes, and the carbon tetrachloride layer was recovered and placed in a 1.0 cm cell. The absorption of the carbon tetrachloride solution was read at 435 nm against a blank prepared in identical fashion

TABLE XIII

QUANTITATIVE EVALUATION OF THE COPPER CONTENT IN $Cu(DPM)_2$-$Be(DPM)_2$ MIXTURES SEPARATED BY FRACTIONAL SUBLIMATION IN THE LARGE SUBLIMATOR

Experiment Designation[a]	Original Copper Content mg.	Copper in Copper Rich Zone mg.	Copper in Beryllium Rich Zone mg.
A	0.86	0.79	0.00
B	1.17	1.12	0.00
C	0.98	0.97	0.00

[a]These designations correspond to those found in Figure 18.

TABLE XIV

QUANTITATIVE EVALUATION OF THE RHODIUM CONTENT IN $Rh(DPM)_3$-$Pt(DPM)_2$ MIXTURES SEPARATED BY FRACTIONAL SUBLIMATION IN THE LARGE SUBLIMATOR

Experiment Designation[a]	Original Rhodium Content mg.	Rhodium in Rhodium Rich Zone mg.	Rhodium in Platinum Rich Zone mg.
A	0.77	0.75	0.00
B	0.62	0.60	0.00
C	0.96	0.96	0.00

[a]These designations correspond to those found in Figure 18.

except for the presence of copper. The concentration was determined by using a calibration curve prepared from the same copper dipivaloylmethane chelate. The calibration curve used is shown in Figure 19 and the results are shown in Tables X and XIII.

b. Rhodium Analysis: The amount of rhodium recovered by sublimation was analyzed by using the method suggested by Ayers (58). The procedure used was identical to that described by Ayers except for minor modifications which are outlined in the following description: The sublimation tube was removed hot, capped, and allowed to cool to room temperature. The tube was then cut at the intervals selected for study and each section was washed with 10-15 ml of aqua regia. The solution was then carefully evaporated to about 3 ml and then diluted with 6 ml of 6N hydrochloric acid. It was again carefully evaporated to about 3 ml and diluted with 15 ml of deionized distilled water. It was again evaporated to 3 ml and diluted to 10 ml in a volumetric flask. Appropriate aliquot portions of the stock solutions were treated with Chlorox and a sodium acetate buffer (58). The dilutions were made so that the final concentration of the analyzed solution would fall between 5 and 25 ppm of rhodium. The solution was allowed to equilibrate for sixty minutes, and the absorption was then read in a 1.0 cm cell at 660 nm against a blank which contained all the components except rhodium. The rhodium concentration was interpolated from a calibration curve prepared by using the pure rhodium chelate. The calibration curve is shown in Figure 20, and the results are shown in Tables XI, XII and XIV.

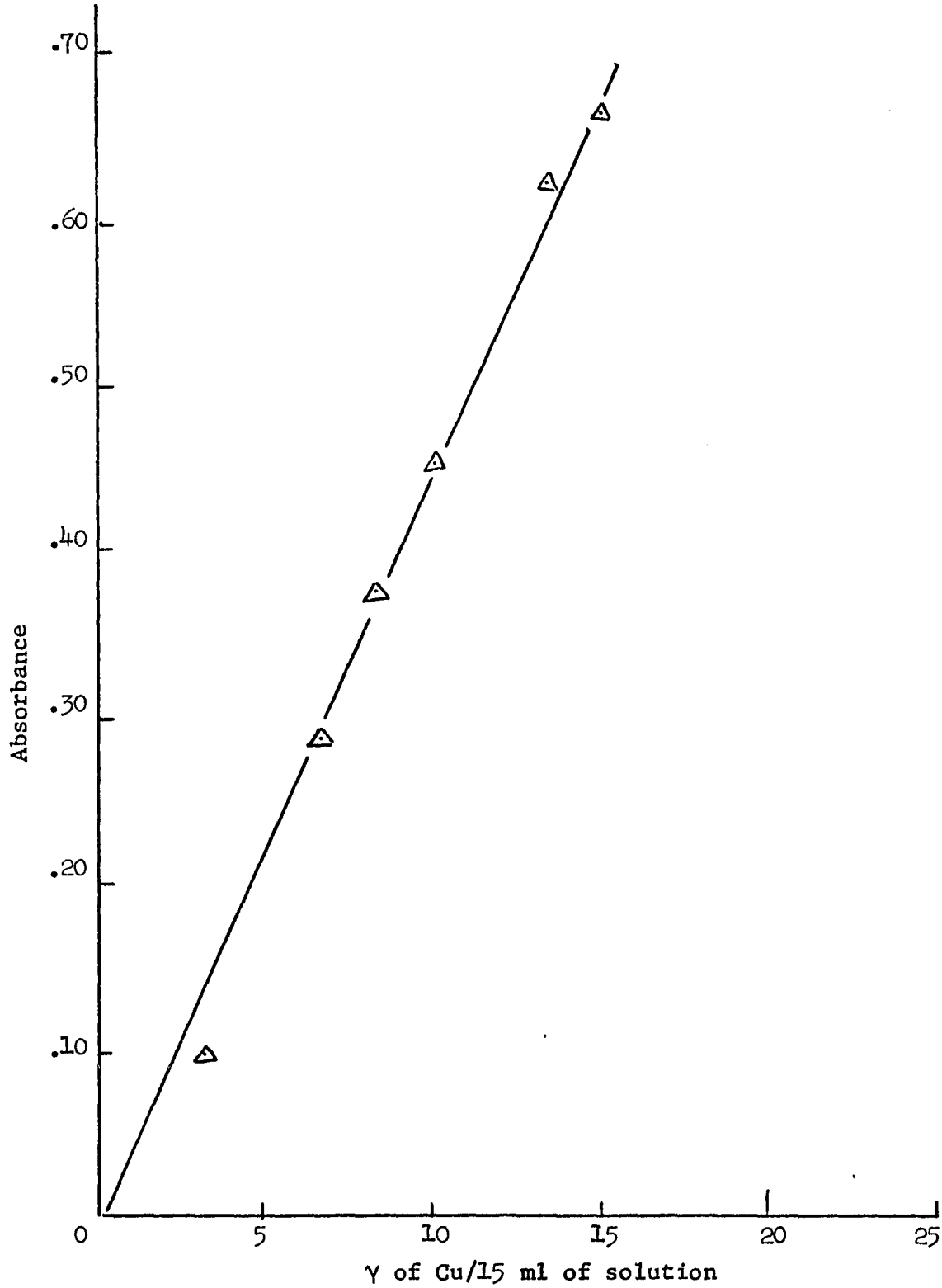


FIGURE 19. Calibration Curve for the Quantitative Determination of Copper

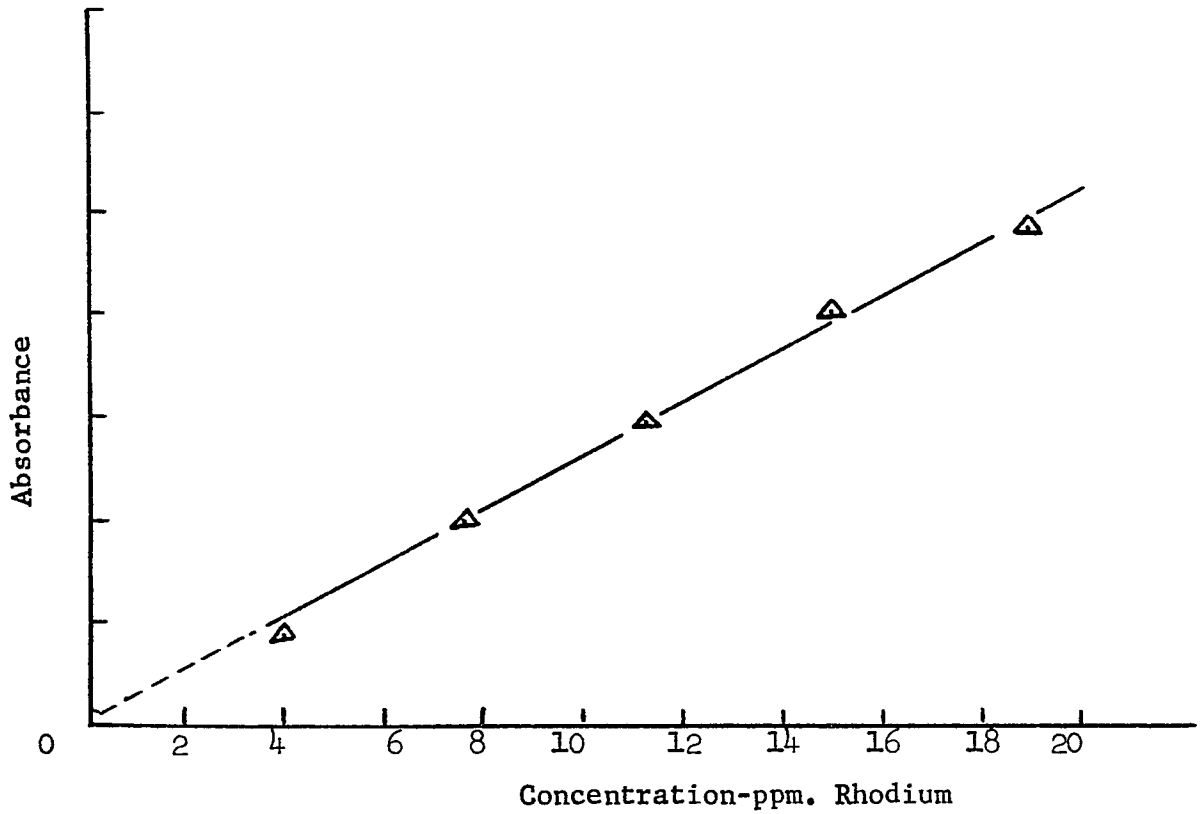


FIGURE 20. Calibration Curve for the Quantitative Determination of Rhodium.

4. Fractional Sublimation of the Metal Chelates of Malonaldehyde

A. Tris-(malonaldehydato)chromium (III). This chelate sublimed without noticeable decomposition in the same region as the chromium (III) chelates of acetylacetone and dipivaloylmethane. This relationship can be seen in Figure 13.

B. Bis-(malonaldehydato)palladium (II). This chelate sublimed with apparent decomposition into two types of condensates. In the region between 170-180°C a smooth, fine grained, shiny palladium metal mirror deposited on the surface of the glass tube. The normal palladium chelate of malonaldehyde deposited in the region between 45-70°C, near the condenser cooled section of the sublimation tube.

To determine which set of conditions would provide the most even and best defined deposits of palladium metal it was decided to change the following parameters: powerstat setting (temperature), air pressure and total pump time. The results of this study are shown in Figure 21.

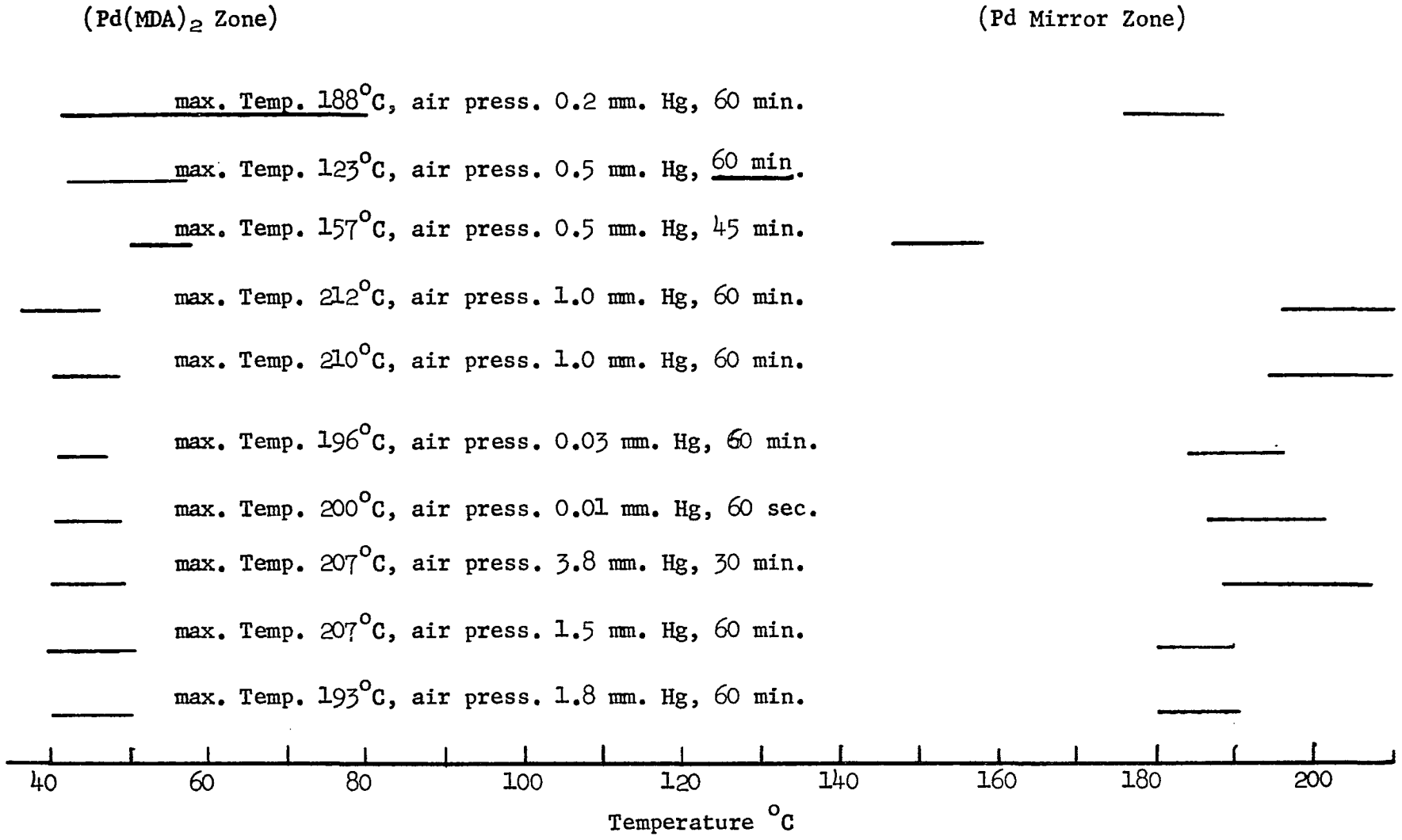


FIGURE 21. Data on the Fractional Sublimation of Bis-(malonaldehydato)palladium (II)

SUMMARY AND CONCLUSIONS

I. Preparation and Characteristics of the Metal Chelates of Dicarbonyl Ligands.

Twenty-two metal chelates of dicarbonyl ligands have been prepared and studied. The methods of preparation of these chelates follow the same procedures for the preparation of chelates in general.

The infrared data (Tables III, IV, and V) on β-dicarbonyl metal chelates confirm some of the trends suggested by Holtzclaw (47) and Nakamoto (45) and suggest some new ones. The infrared spectra of the metal chelates of dipivaloylmethane (Table III) do not show much variation in the absorption bands of the fingerprint region when the metal is changed. This criterion can be used successfully in the characterization of true β-dicarbonyl chelates. Comparing the spectra of β-dicarbonyl chelates of palladium and chromium (Tables VI and VII), we can see that variation in the C=C and C=O absorption bands indicates that as we change the substituent α to the carbonyl carbon from t-C_4H_9 to CH_3 to H, the strength of the C=C and C=O bonds increase . These changes could be attributed to inductive (45) and steric effects.

The NMR data (Table VI) for different dipivaloylmethane metal chelates indicate great similarities in the chemical shift values for similar protons, and no clear trend was found to relate the shift variations to the bound metal. No definite trends could be found by comparing the chemical shift values (Table VII) of various β-dicarbonyl chelates of palladium. The NMR shift values reported

for the bis-(malonaldehydato)palladium (II) chelate are the first ones ever reported for a chelate of malonaldehyde.

Slight discrepancies between the melting points found and those reported (42) can be attributed to differences in equipment used and in the method of purification. Discrepancies found between theoretical and experimental carbon and hydrogen analysis values can be attributed to the nature of the chelates and to the difficulty in purifying the non-volatile members of this group. Communications from commercial analytical laboratories have indicated that β-diketone metal chelates frequently give erroneous carbon-hydrogen analysis.

A key step in the preparation of many of these chelates was the control of the various equilibria that exist in the solutions. The difficulty in preparing metal chelates of malonaldehyde could be partly due to equilibria of the type shown in Figure 22. The authors (28-32,34-39) who have studied malonaldehyde in detail have not reported the existence of the hydrolysis products of malonaldehyde and their metal chelates. As formaldehyde and acetaldehyde hydrate readily (59-62), and to a great extent to the diol product, it would be logical to assume that malonaldehyde would follow the same pattern. If this assumption is true, the gem-diols would have to be considered, along with malonaldehyde, as products of the hydrolysis of tetraalkoxypropanes. The NMR and infrared data obtained from the solid compounds isolated from the aqueous solutions of malonaldehyde-metal ions did not provide any information that could be used to determine the structure of the products.

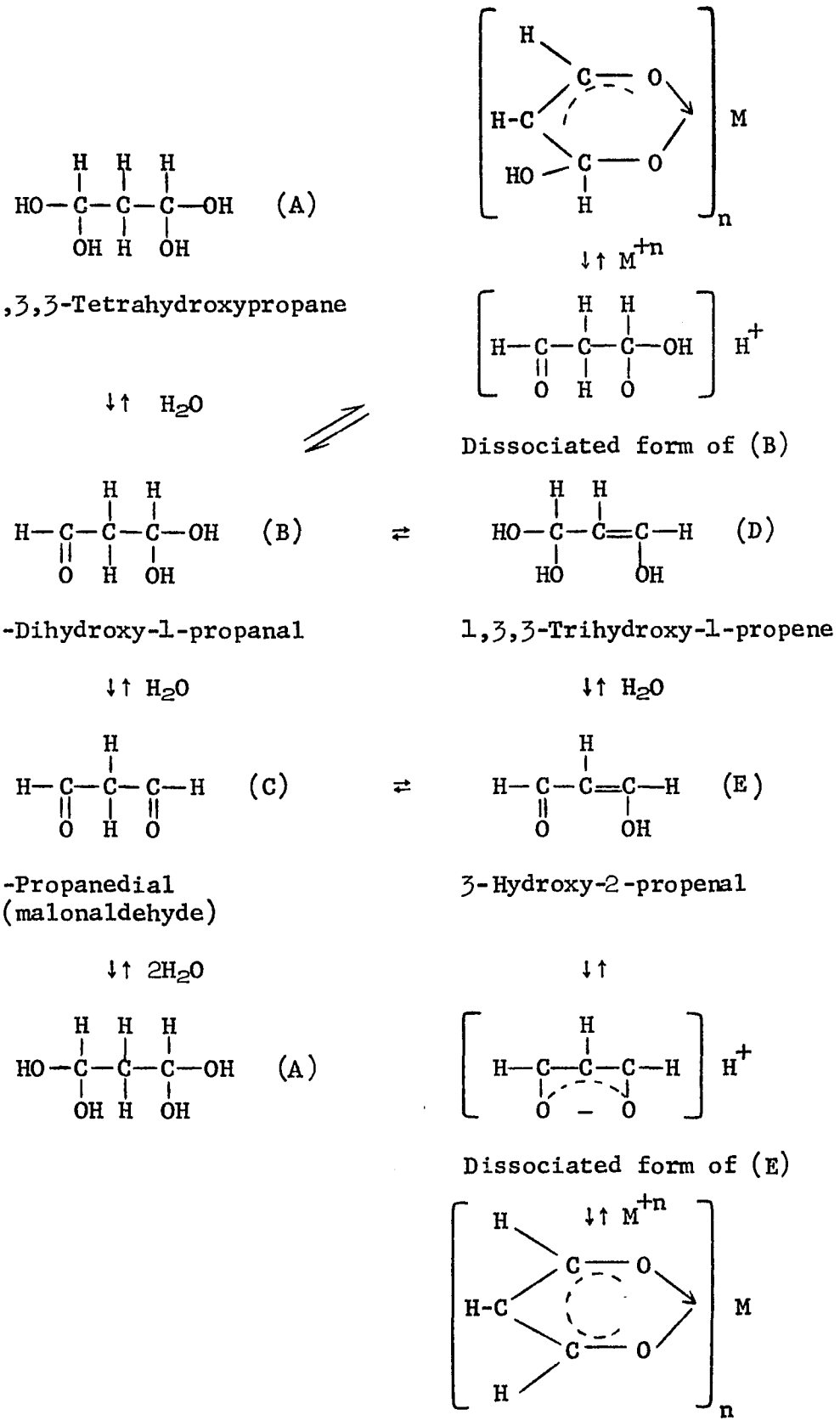


FIGURE 22. Selected Equilibria of Malonaldehyde and Its Metal Chelates

II. New Oxidation System

Four different types of alcohols were involved in the study of the oxidation of alcohols to aldehydes. Their vapors were exposed to one reagent and two catalysts in the new oxidation system (Figures 4, 5, 6, and 7). The results (Table VIII) indicate that the system produces aldehydes in yields comparable to those obtained by more complicated and expensive systems. The oxidation of alcohols which were difficult to dehydrate or cleave, gave the aldehyde in mixtures which were easy to resolve. Alcohols with the OH group attached to straight chain parent groups gave complex mixtures of oxidation, reduction and cleavage products. The oxidation of 1,3-propanediol produced malonaldehyde in poor yields (Table VIII) and as a complex mixture which was not completely resolved.

III. Volatility and Separability of the Metal Chelates of β-Dicarbonyl Ligands

Most of the true metal chelates of β-dicarbonyl compounds appear to be stable and volatile during sublimation at low pressure. The assumption that individual sublimation data (Figure 12) can be used to predict the separation of mixtures is confirmed by the qualitative and quantitative data presented in Tables X, XI, XII, XIII, XIV and Figures 16, 17, and 18. On the basis of these data, it is proposed that the following separations of mixtures of dipivaloylmethane chelates are feasible by fractional sublimation.

1. Best Separations

A. The following binary and ternary mixtures probably can be resolved quantitatively because there is no overlap of the individual condensation temperature zones and each chelate is quantitatively sublimed.

$Be(DPM)_2$ - $Cu(DPM)_2$
$Be(DPM)_2$ - $Cr(DPM)_3$
$Be(DPM)_2$ - $Ni(DPM)_2$
$Be(DPM)_2$ - $Th(DPM)_4$
$Be(DPM)_2$ - $Y(DPM)_3$
$Zr(DPM)_4$ - $Al(DPM)_3$
$Zr(DPM)_4$ - $Cr(DPM)_3$
$Zr(DPM)_4$ - $Co(DPM)_3$
$Zr(DPM)_4$ - $Mg(DPM)_2$
$Zr(DPM)_4$ - $Mn(DPM)_3$
$Be(DPM)_2$ - $Cr(DPM)_3$ - $Zr(DPM)_4$

B. The following binary and ternary mixtures probably can be resolved quantitatively but there would not be a 100% recovery of some components. A quantitative recovery is hindered because some of the chelates do not sublime quantitatively in all cases.

$Be(DPM)_2$ - $Ce(DPM)_4$
$Be(DPM)_2$ - $La(DPM)_3$
$Be(DPM)_2$ - $Hg(DPM)_2$
$Zn(DPM)_2$ - $Ce(DPM)_4$
$Zn(DPM)_2$ - $La(DPM)_3$
$Zn(DPM)_2$ - $Hg(DPM)_2$
$Zn(DPM)_2$ - $Th(DPM)_4$
$Zn(DPM)_2$ - $Zr(DPM)_4$
$Rh(DPM)_3$ - $Ce(DPM)_4$
$Rh(DPM)_3$ - $La(DPM)_3$
$Rh(DPM)_3$ - $Hg(DPM)_2$
$Rh(DPM)_3$ - $Th(DPM)_4$
$Rh(DPM)_3$ - $Zr(DPM)_4$
$Co(DPM)_2$ - $Ce(DPM)_4$
$Co(DPM)_2$ - $La(DPM)_3$
$Co(DPM)_2$ - $Hg(DPM)_2$
$Co(DPM)_2$ - $Th(DPM)_4$
$Co(DPM)_2$ - $Zr(DPM)_4$

$Co(DPM)_3$ - $Ce(DPM)_4$
$Co(DPM)_3$ - $La(DPM)_3$
$Co(DPM)_3$ - $Hg(DPM)_2$
$Al(DPM)_3$ - $Ce(DPM)_4$
$Al(DPM)_3$ - $La(DPM)_3$
$Al(DPM)_3$ - $Hg(DPM)_2$
$Cr(DPM)_3$ - $Ce(DPM)_4$
$Cr(DPM)_3$ - $La(DPM)_3$
$Cr(DPM)_3$ - $Hg(DPM)_2$
$Mg(DPM)_2$ - $Ce(DPM)_4$
$Mg(DPM)_2$ - $La(DPM)_3$
$Mg(DPM)_2$ - $Hg(DPM)_2$
$Mn(DPM)_3$ - $Ce(DPM)_4$
$Mn(DPM)_3$ - $La(DPM)_3$
$Mn(DPM)_3$ - $Hg(DPM)_2$
$Fe(DPM)_3$ - $Ce(DPM)_4$
$Fe(DPM)_3$ - $La(DPM)_3$
$Fe(DPM)_3$ - $Hg(DPM)_2$
$Fe(DPM)_3$ - $Zr(DPM)_4$
$Cu(DPM)_2$ - $Ce(DPM)_4$
$Cu(DPM)_2$ - $La(DPM)_3$
$Ni(DPM)_2$ - $Ce(DPM)_4$
$Ni(DPM)_2$ - $La(DPM)_3$
$Pt(DPM)_2$ - $Ce(DPM)_4$
$Pt(DPM)_2$ - $La(DPM)_3$
$Pd(DPM)_2$ - $La(DPM)_3$
$Be(DPM)_2$ - $Cr(DPM)_3$ - $Ce(DPM)_4$
$Be(DPM)_2$ - $Cr(DPM)_3$ - $La(DPM)_3$
$Be(DPM)_2$ - $Cr(DPM)_3$ - $Hg(DPM)_2$
$Be(DPM)_2$ - $Cu(DPM)_2$ - $Ce(DPM)_4$
$Be(DPM)_2$ - $Cu(DPM)_2$ - $La(DPM)_3$
$Be(DPM)_2$ - $Ni(DPM)_2$ - $Ce(DPM)_4$
$Be(DPM)_2$ - $Ni(DPM)_2$ - $La(DPM)_3$
$Be(DPM)_2$ - $Pt(DPM)_2$ - $Ce(DPM)_4$
$Be(DPM)_2$ - $Pt(DPM)_2$ - $La(DPM)_3$
$Be(DPM)_2$ - $Pd(DPM)_2$ - $La(DPM)_3$

2. Other Proposed Separations

A. The following binary and ternary mixtures probably can be resolved but not quantitatively because there is some overlap in the boundary area of the condensation zones. The chelates recovered are sublimed quantitatively.

$Be(DPM)_2$ - $Mg(DPM)_2$
$Be(DPM)_2$ - $Mn(DPM)_3$
$Be(DPM)_2$ - $Pd(DPM)_2$
$Cu(DPM)_2$ - $Zr(DPM)_4$
$Ni(DPM)_2$ - $Zr(DPM)_4$
$Be(DPM)_2$ - $Cr(DPM)_3$ - $Th(DPM)_4$
$Be(DPM)_2$ - $Cu(DPM)_2$ - $Zr(DPM)_4$
$Be(DPM)_2$ - $Mg(DPM)_2$ - $Th(DPM)_4$
$Be(DPM)_2$ - $Mg(DPM)_2$ - $Zr(DPM)_4$
$Be(DPM)_2$ - $Mn(DPM)_2$ - $Zr(DPM)_4$
$Be(DPM)_2$ - $Ni(DPM)_2$ - $Zr(DPM)_4$

B. The following binary and ternary mixtures probably can be resolved but not quantitatively because there is some overlap in the boundary area of the condensation zones. The chelates recovered are not 100% sublimed in all cases.

$Be(DPM)_2$ - $Fe(DPM)_3$
$Zn(DPM)_2$ - $Pt(DPM)_2$
$Zn(DPM)_2$ - $Y(DPM)_3$
$Rh(DPM)_3$ - $Pt(DPM)_2$
$Rh(DPM)_3$ - $Th(DPM)_4$
$Al(DPM)_3$ - $Th(DPM)_4$
$Cr(DPM)_3$ - $Th(DPM)_4$
$Mg(DPM)_2$ - $Th(DPM)_4$
$Pd(DPM)_2$ - $Ce(DPM)_4$
$Be(DPM)_2$ - $Fe(DPM)_3$ - $Ce(DPM)_4$
$Be(DPM)_2$ - $Fe(DPM)_3$ - $La(DPM)_4$
$Be(DPM)_2$ - $Fe(DPM)_3$ - $Hg(DPM)_2$
$Be(DPM)_2$ - $Fe(DPM)_3$ - $Zr(DPM)_4$
$Be(DPM)_2$ - $Mg(DPM)_2$ - $Ce(DPM)_4$
$Be(DPM)_2$ - $Mg(DPM)_2$ - $Hg(DPM)_2$
$Be(DPM)_2$ - $Pd(DPM)_2$ - $Ce(DPM)_4$
$Be(DPM)_2$ - $Mg(DPM)_2$ - $La(DPM)_3$
$Be(DPM)_2$ - $Mn(DPM)_3$ - $Ce(DPM)_4$
$Be(DPM)_2$ - $Mn(DPM)_3$ - $La(DPM)_3$
$Be(DPM)_2$ - $Mn(DPM)_3$ - $Hg(DPM)_2$

3. Separations with Non-Volatile Chelates

The dipivaloylmethane chelates of barium (II), cadmium (II), calcium (II), and strontium (II) are not volatile under the present sublimation conditions and can be easily separated from those volatile

chelates which are 100% sublimed. These volatile chelates are: aluminum (III), beryllium (II), chromium (III), cobalt (III), copper (II), magnesium (II), manganese (III), nickel (II), palladium (II), platinum (II), thorium (IV), yttrium (III), and zirconium (IV).

4. Separations Predicted Directly or Indirectly from J. Chiang Thesis Data.

To be able to use the data from Chiang's (17) thesis, the author sublimed representative members of the dipivaloylmethane metal chelates of Group IIIB and then interpolated these data with his own. With this information one can predict that the following separations will also probably take place.

$Sc(DPM)_3$ - $Th(DPM)_4$
$Sc(DPM)_3$ - $Nd(DPM)_3$
$Sc(DPM)_3$ - $Pr(DPM)_3$
$Sc(DPM)_3$ - $Ce(DPM)_4$
$Sc(DPM)_3$ - $La(DPM)_3$
$Tm(DPM)_3$ - $Th(DPM)_4$
$Tm(DPM)_3$ - $Nd(DPM)_3$
$Tm(DPM)_3$ - $Pr(DPM)_3$
$Tm(DPM)_3$ - $Ce(DPM)_4$
$Tm(DPM)_3$ - $La(DPM)_3$
$Yb(DPM)_3$ - $Th(DPM)_4$
$Yb(DPM)_3$ - $Nd(DPM)_3$
$Yb(DPM)_3$ - $Pr(DPM)_3$
$Yb(DPM)_3$ - $Ce(DPM)_4$
$Yb(DPM)_3$ - $La(DPM)_3$

Chiang's (17) sublimation-condensation zones for the chelates coincide in temperature with the ones found in this study and they follow the same sequence. The lanthanum (III) condensation zone is found at the highest temperature followed by thorium (IV), zirconium (IV), and yttrium (III). None of Chiang's zones extends any lower in

temperature than yttrium (III), and it can be assumed that as yttrium (III) has been predicted separable from beryllium (II), all of Chiang's binary mixtures can be separated also from beryllium (II) and probably from zinc (II) and rhodium (III). If we include again the non-volatile chelates, the proposed separation of ternary mixtures could be enhanced to quaternary.

The cold end limit for the cerium (IV), lanthanum (III), and thorium (IV) zones is similar to that of the neodymium (III) and praseodymium (III) zones; so it is probable that any chelate that can be separated from the former chelates can also be separated from the latter. This prediction means that aluminum (III), chromium (III), cobalt (II), iron (III), magnesium (II), rhodium (III), and zinc (II) may also be separated from neodymium (III), and praseodymium (III).

The metal chelates of lutetium (II), erbium (III), holmium (III), dysprosium (III), yttrium (III), gandolium (III), europium (III) and samarium (III) sublime in the same temperature range as ytterbium (III) and any separations predicted for this chelate can also be achieved for the others.

The fractional sublimation data (Figure 14) for different β-dicarbonyl ligands of chromium show no significant differences in volatility when the substituent α to the carbonyl carbon is changed from $\underline{t}$-C_4H_9 to CH_3 to H. The fractional sublimation data (Figure 13) for selected β-dicarbonyl chelates of palladium show no significant differences in volatility for the palladium chelates of acetylacetone and dipivaloylmethane; however the malonaldehyde chelate of palladium

shows the formation of two condensation zones; one is a palladium metal mirror and the other is the chelate. The possibility of preparing smooth palladium mirrors at moderate temperatures (Figure 22) has potential useful applications in catalysis and spectroscopy.

IV. General Summary and Suggestions for Future Work

The study has produced considerable and important data concerning the preparation and volatility of β-dicarbonyl metal chelates. A new oxidation system was designed, and the Berg sublimator was modified to include a more selective temperature gradient control. These two systems were tested, and the data (Tables VIII, XIII, XIV) indicate that both systems can be used advantageously over their earlier counterparts. The formation of a palladium mirror at low temperatures has opened the field for potential deposition applications of a metal surface onto materials which would be decomposed at high temperatures.

This investigation has proven that there is still much to be learned from the β-dicarbonyls and their metal chelates. The following are some areas of study that should be investigated to complement this work:

a. New metal chelates of β-dicarbonyl ligands especially those of malonaldehyde should be prepared and studied to determine if other metal mirrors can be produced by their low temperature sublimation.

b. The study of the sublimation characteristics of bis-(malonaldehydato)palladium (II) should be continued to determine the full potential of the palladium mirror deposition.

c. The oxidation system and the longer version of the Berg sublimator should be further evaluated to determine their full potential.

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VITA

Nicolas M. Herrera, was born in Habana, Cuba, on January 19, 1932. He received his elementary and high school education in the Christian Brothers School in Habana, Cuba, from which he graduated Summa Cum Laude in 1949.

He did his undergraduate work at Rensselaer Polytechnic Institute, Troy, New York, from which he received the Bachelor of Science degree in 1953. He received the equivalent of a Masters degree in Engineering from the University of Habana in 1954.

He worked as a geological engineer in Cuba, United States, and Europe from 1954 to 1961.

In 1962 he started his graduate studies in chemistry at Birmingham Southern College, Birmingham, Alabama and graduated from that institution with the degree of Master of Science in 1966.

In 1964 he entered the Graduate School of Louisiana State University, Baton Rouge, Louisiana, on the long range Ph.D. Program sponsored by the Chemistry Department. In 1971 he received a National Science Foundation Science Faculty Fellowship to complete the last phase of his education. He is now a candidate for the degree of Doctor of Philosophy.

He is Associate Professor of Chemistry at St. Bernard College, Cullman, Alabama and is presently on leave from that institution. He is married to the former Dr. Martha E. Rosado of Las Villas, Cuba and has four children, Lorenzo, Nicolas, Martha and Mario.

EXAMINATION AND THESIS REPORT

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Major Field: Chemistry

Title of Thesis: A Study of the Volatility of the Metal Chelates of Dipivaloylmethane and Related Dicarbonyl Compounds

Approved:

Eugene W. Berg
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

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Date of Examination:

October 28, 1971